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The adsorption of secondary effluent and carbohydrates by carbon

Charles A. Burchett
Lehigh University

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THE ADSORPTION OF SECONDARY EFFLUENT
AND CARBOHYDRATES BY CARBON

by

Charles A. Burchett

A Thesis

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Chemical Engineering

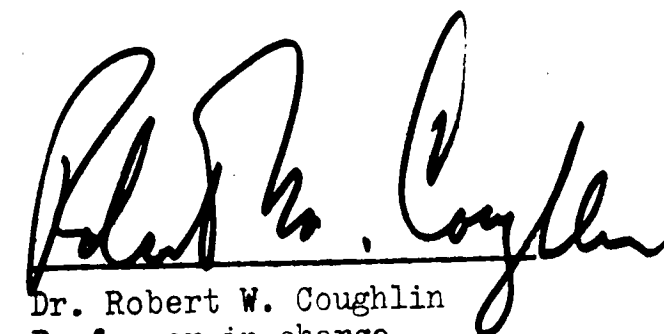
Lehigh University

1970

CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the Degree of Master of Science in Chemical Engineering.

27 January 1970
(date)


Dr. Robert W. Coughlin
Professor in charge

Dr. Curtis Clump
Acting Chairman of the Department
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ABSTRACT

Activated carbon has for a long time been known to possess high adsorption capacities. However, LC325 (Columbia Carbon Div. of Union Carbide) activated carbon proved to have poor adsorption characteristics for reducing the chemical oxygen demand of sewage effluent.

On the other hand, a carbohydrate (dextrose) usually present within a typical municipal waste secondary effluent was found to adsorb readily from pure solution onto the carbon surface. It was also found that addition of acidic oxide groups to the carbon surface measurably reduced the adsorption capacity of the carbon for dextrose. However, the original adsorption capacity of the carbon could almost be completely restored by reducing the concentration of these groups.

Kinetic studies of adsorption rate showed low activation energies of 785 cal/mole for the oxidized carbon and 2290 cal/mole for the washed unoxidized carbon, although the oxidized carbon displayed a far lower rate of adsorption than did the same carbon before oxidation. A satisfactory explanation was not reached to explain the apparent lower activation energy of the oxidized carbon.

INTRODUCTION

The disposal of wastes has always constituted a serious problem to man. Only recently has considerable research been undertaken to study the treatment of waste water. In particular, the tertiary treatment of sewage waste treatment plant effluent is becoming increasingly important. The exact chemical composition of this effluent is highly variable and virtually unknown, but it is certain to contain proteins, amino acids, and carbohydrates.

The pollution strength of industrial and domestic wastes is usually measured by the biochemical oxygen demand (B.O.D.) and by the chemical oxygen demand (C.O.D.). The latter test allows measurement of waste in terms of total quantity of oxygen required for oxidation to carbon dioxide and water. It is based upon the fact that all organic compounds, with a few exceptions, can be oxidized by the action of strong oxidizing agents under acid conditions.

One of many materials which is capable of removing organic contaminants from waste water or reducing C.O.D. is carbon. Although extensive study has been done on the adsorption characteristics of many organic pollutants such as phenols, insecticides, chlorinated paraffins and synthetic dyes, very little work has been done with simple carbohydrates. It is the purpose of this report to

OBJECTIVE

The objective of this research was to study the use of carbon to adsorb C.O.D. from actual sewage effluent. In addition, the adsorption of some typical carbohydrates (known to be present in typical secondary waste water effluent) onto the carbon surface from pure aqueous solution was also examined. It was of interest to determine the effect of acidic surface oxides on the adsorption of these various carbohydrates onto the carbon surface from pure aqueous solution.

SELECTION OF ADSORBATES

The sewage effluent employed in the work came from Bethlehem's trickle-filter sewage disposal plant. This was primarily due to the plant's accessible locale, as fresh effluent was needed every few days.

The two carbohydrates chosen to be studied were: lactose, a disaccharide and dextrose, a monosaccharide. Both are common carbohydrates found in sewage effluent and both lend themselves to fast and simple quantitative analysis.

The two adsorbates, lactose and dextrose, were of reagent grade obtained from J. T. Baker Chemical Company.

SELECTION OF ADSORBENTS

The two types of carbon used were: a) activated carbon "Columbia LC325" (Union Carbide Corporation); and b) "Calgon Filtrasorb 300" (Calgon Corporation).

Columbia LC325 was selected because extensive work has already been ~~done~~ with the carbon. (8,15,16) It is also an activated carbon which possesses high-adsorption characteristics.

Calgon Filtrasorb 300 was received from the manufacturer in a 5 lb. sample composed of particle sizes, ranging from 6/7 U. S. Standard sieve size to fine powder. The larger particle sizes were particularly useful in kinetic studies since it was relatively easy to separate the carbon from the sugar solution.

ANALYTICAL PROCEDURES

A. Analysis of Surface Oxides

The determination of the acidic surface oxide groups consisted of equilibrating 0.500 grams of the sample with 50.0 ml. each of 0.10 Normal NaOC_2H_5 , NaOH , Na_2CO_3 and NaHCO_3 solution for three days. A 10 ml. aliquot is then pipetted out and titrated with 0.05 N HCL , using

phenolphthalein as an indicator in case of NaOC_2H_5 and NaOH , and methyl orange in case of Na_2CO_3 and NaHCO_3 .

B. Analysis of Adsorbates Concentration

The standard Chemical Oxygen Demand technique (11) was employed in the analysis of the sewage effluent. The concentration of the two carbohydrates used was done by a Polarimeter - providing a very simple form of analysis.

C. Determination of Surface Area

The surface area of Columbia LC325 had been previously determined using B. E. T. surface area methods by Ricardo N. Tan (12) (see Table 4 , page 28) The surface area of CF300 was supplied by the Calgon Corporation. (see Table 7, page 31).

EXPERIMENTAL PROCEDURES

A. Preparation of the Adsorbates

The sewage effluent was obtained every two days from the Bethlehem plant because for any longer period of time, the effluent would start to deteriorate rapidly.

Stock solutions, of both dextrose and lactose, were

prepared at standard concentrations of 100 grams per liter by weighing appropriate quantities of chemicals and dissolving them in suitable volumes of double-deionized water. Various concentrations were then obtained by pipetting out known quantities of stock solution and diluting them to known volumes. The concentrations used in an isotherm run are listed in Appendix A.

B. Preparation of the Adsorbents

The carbon was first stirred for 24 hours with 0.1 Normal HCL to remove alkaline impurities, and then washed thoroughly with double-deionized water. Samples were then dried overnight at 110°C before they were used in any additional experiments or preparations. These samples will be referred to as washed carbon.

Oxidized carbon samples were obtained by wet oxidation of the washed carbon. Oxidation was carried out by stirring approximately 20 grams of washed carbon in 500 ml. of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ammonium persulfate solution for three days at room temperature. These oxidized samples were then washed thoroughly for 24 hours with double-deionized water and dried at 110°C for 24 hours. These samples will be referred to as oxidized carbon.

Saturated ammonium persulfate was used to oxidize

LC325 and 0.4 and 0.8 molar was used to oxidize CF300 -- each for a period of 3 days. The low concentration of ammonium persulfate was used with the CF300 to preserve the original size of the particles.

Further preparation consisted of chemically reducing part of the oxidized samples. Only the LC325 was reduced by mixing about 15-20 grams of the oxidized samples with zinc amalgam (which consisted of 50 grams of 10 mesh granular zinc covered with 10 ml. of mercury) and then covering the mixture with about 150 ml. of concentrated HCL. The reduction was carried on for one week and was followed by thoroughly washing the carbon with doubly deionized water and drying for 24 hours at 110°C. These samples will be referred to as oxidized-reduced carbon.

C. Procedures for Adsorption Studies

Adsorption studies using the sewage effluent were conducted using the standard Chemical Oxygen Demand technique. (11)

The C.O.D. was determined before and after carbon addition; a blank and sample run were made at the same time. Preliminary runs suggested that the appropriate amount of carbon to be used was about 0.005 g of LC325 washed carbon to 20 ml. of effluent. (Here the word appropriate refers to the

amount of carbon which will produce reasonably precise and accurate results.) All sample and blank runs were conducted in the Water Bath Shaker (Eberbach Corporation) at a temperature of 30°C for 1.0 hour.

Adsorption studies using dextrose and lactose were conducted using pure aqueous solutions. Working solutions of different concentrations were prepared from the standard stock solution of 100 grams per liter (see Appendix A for concentrations used). From these working solutions, 50 ml, was pipetted out into the 16 oz. jars with polyethelene caps. Preliminary tests determined the appropriate amount of carbon to be 1.0 grams. And this amount was added to each of these jars. The bottles were then put into the shaker (speed control 4,5) and left to equilibrate at 30°C for 1.0 hour. Some initial kinetic studies determined an equilibrium time of one hour. (see Figure 5).

On equilibration of one hour, the solutions were filtered using Whatman No. 42 filter paper in the case of LC325 and No. 2 for CF300. Because LC325 is a very fine powder it was necessary to use an extra fine filter paper. Even then, it was sometimes necessary to filter twice to obtain a clear filtrate. In the case of CF300, the larger particles permitted the use of a coarser filter paper. After

filtration, the residual concentration was determined by using the Polarimeter. In using the Polarimeter, it is important to have a clear solution. And this is the main reason for the careful filtration procedure. A computer program (see Appendix A) was developed for converting the optical rotation data recorded from the Polarimeter to residual concentration and adsorption data.

A. PROCEDURE FOR KINETIC STUDIES

Kinetic studies were conducted only with dextrose and CF300 carbon. A working solution of 50 g/l of dextrose was used. 50 ml. of this solution was added to each 16 oz. jar. The jars were allowed to stand for 1.0 hour in the shaker to equilibrate to the desired temperature. One gram of carbon was then added, carefully noting the time. The solutions were filtered every 10 minutes using filter paper No. 2.

An alternative procedure involved conducting the adsorption in the Polarimeter cell itself. The cell was equipped with a water jacket to prevent variations in temperature. After 15 ml. of dextrose solution was added to the cell and an equilibrium temperature had been reached, 0.5 grams of carbon were added, carefully noting the time.

The cell was shaken every 2½ minutes and a reading was taken every 10 minutes. The experimental results agreed well with those of the first procedure. (see Figure 11).

RESULTS AND DISCUSSIONS

A. Sewage Effluent

Batch adsorption tests showed an initial C.O.D. of 133 mg/l declining to 52 mg/l after about a day deterioration period. Using .005 grams of LC325 washed activated carbon to 20 ml. effluent a 14% reduction in the C.O.D. was obtained. (see Table I).

As seen in Figure 20 the results of L.D. Friedman (8) of FMC Corporation showed a Freundlich isotherm for the amount of total oxidizable carbon (TOC) LC325 adsorbed from secondary effluent. Oxidation of the carbon surface apparently reduced the adsorption capacity of the carbon. However, the adsorption capacity of the carbon was not restored by reducing the oxidized sample. Friedman further reports that black Pearl Carbon P607 (Cabot Corporation) in Figure 19 showed similar results to LC325 carbon. On the other hand, Darco 851 carbon (Atlas Chemical Company) showed a reasonable amount of adsorptive capacity. (see Figure 18.)

B. Lactose Adsorption Studies

Initial adsorption studies using lactose hydrate proved unsuccessful. Extreme scatter in the data was found, making it virtually impossible to obtain a smooth curve. (see page 56). The probable explanation for these results is that lactose hydrate is a disaccharide and any trace of HCl from the washing process will cause hydrolysis yielding monosaccharides. At this point work was discontinued.

C. Dextrose Adsorption Studies

Initial adsorption studies of dextrose on LC325 washed carbon resulted in a Langmuirian type isotherm with a plateau value of approximately 1.0 micro moles of sugar adsorbed per gram of carbon as shown in Figure 1. The oxidized LC325 carbon reduced the plateau value to approximately 0.4 micro moles of dextrose adsorbed per gram of carbon. It appears that the effect of oxidation reduced the adsorption capacities of carbon for dextrose by a factor of about 2.5 on a per gram basis. To check whether the surface area of the oxidized samples had not changed the adsorption data was expressed on a per unit surface area basis by using the B.E.T. specific surface area data. The adsorption isotherms

of Figure 2 proved to be basically identical in shape, suggesting that difference in adsorption capacities were not due to differences in surface area.

In trying to restore the oxidized carbons' adsorption capacities using aqueous chemical reduction, the oxidized-reduced carbon showed a plateau value of approximately 0.9 micromoles/ gram comparing very well with 1.0 micromoles/ gram for the original washed carbon (see Figure 1). Therefore, aqueous reduction of the oxidized carbon restored adsorption capacity almost completely.

In computing plateau values and monolayer coverages, the most convenient form of the Langmuir equation is:

$$\frac{c}{V} = \frac{1}{bV_m} + \frac{c}{V_m}$$

where c = equilibrium concentration

V = amount of solute adsorbed per unit weight of adsorbent

V_m = value of V for complete monolayer coverage

b = constant in Langmuir equation, expressive of energy of interaction with surface

A plot of c/V versus c shows a straight line with the reciprocal of the slope equal to V_m . (see Figure 3).

The cross sectional surface area of the dextrose molecule lying flat was calculated from the projected surface area of its molecular model (Fisher Atom Model Kit) to be about 50 Angstroms squared. The approximate surface coverages at the Langmuir plateau were calculated using this value and V_m and are listed in Table III. The surface area coverages, ranging between 15-45%, suggest that adsorption was well below the monolayer region at the plateau of the Langmuirian plot.

Adsorption studies using dextrose on CF300-washed (particle size range = 1.41 - 1.68 mm) also resulted in Langmuirian type isotherms. In Figure 4, a plateau value of approximately .65 millimoles of dextrose adsorbed per gram of carbon can be seen. This lower plateau for CF300 as compared to LC325 reflects the much larger particle size of the CF300 carbon and suggests that dextrose molecules could not penetrate into the interior of the large particles in the one-hour equilibration time. LC325 carbon is an activated carbon with particle diameters approximately 0.05 mm, whereas the particle sizes of CF300 for the data in Figure 4 ranged from 1.41 - 1.68 mm indicating a smaller surface area.

Effects of particle size (or external surface area) on adsorption capacity were studied for both

CF300-acid-washed and CF300-oxidized. The CF300-acid-washed carbon showed a gradual increase in adsorption capacity as particle diameters changed from 3.095 mm to .2735 mm, followed by a sharp increase from about 0.5 mm to 0.06 mm. The final adsorption value for CF300 of particle diameter comparable to those of LC325 activated carbon showed equal adsorption capacities. (see Figure 6). This reflects the roughly comparable B.E.T. areas of the two types of carbon. As shown in Figure 6, the adsorption capacity of the oxidized CF300 (carbon was sieved after oxidation) does not increase significantly over the same particle diameter range, although the shape of the curve is basically the same. This may indicate that the acidic oxygen groups on the carbon surface do, to some extent, reduce the adsorption capacity or the ability of the dextrose molecule to penetrate inside the pores. As the external surface area is greatly increased so is the adsorption capacity, indicating a dependency more on external than on internal surface area. Pore diffusion limitation certainly contributes significantly to the decreased adsorption capacity, because the same equilibrium time was used in all the experiments described above. Further work is presently being conducted on the CF300 oxidized carbon to investigate equilibrium time and adsorption isotherms. (7)

D. KINETIC STUDIES

Kinetic studies were conducted using CF300 washed carbon and CF300 oxidized carbon. In the oxidation of the washed carbon it was necessary to maintain a constant external surface area in order to tell what effect the concentration of acidic surface oxide groups had on the adsorption capacity of the carbon. Concentrated solutions of ammonium persulfate (2.5 molar) with long contact times (7 days) showed visible degradation of the carbon surface. However, very dilute solutions for short contact times had no real oxidizing power. For these reasons, dilute solutions were used (0.4 - 0.8 molar) for a contact time of 3 days. For this treatment no visible degradation of the carbon surface was apparent. B.E.T. surface area measurements were not taken after oxidation to insure a constant B.E.T. surface area. However, assuming a constant B.E.T. surface area, Figure 16 shows that the adsorption rate decreases with an increase in the amount of acidic surface oxide groups present.

The effect of external surface area on the adsorption rate was also studied. As shown in Figure 15, there is a large increase in the adsorption rate per gram as particle diameter decreases from 2.605 mm to 0.651 mm. This indicates the larger external surface area of the smaller particle and may

also indicate that a large percentage of the adsorption takes place on the external surface of the carbon as well as within the pores.

Further work involved the determination of activation energies for adsorption using the washed and oxidized CF300 carbon of a single narrow particle size range (2.38 - 2.83 mm). Initial rates of adsorption for both carbon types revealed a linear decrease for the first 30 minutes and a gradual leveling off in 1.0 hours equilibrium time. All values of the rate constant were determined from the initial slope of concentration plotted versus the square root of time in hours. (see Appendix A for calculation). As shown in Table II, the rate constant for the washed carbon was about twice that for the oxidized carbon. The determination of the activation energy for the washed carbon, as shown in Figure 9, was 2290 cal/mole. A comparison of this and the activation energy for the oxidized carbon, (785 cal/mole) (Figure 19) reveals an interesting problem. It would be expected that the oxidized carbon would have a higher activation energy than the washed carbon, but just the opposite is true. (see Table V).

One possible explanation may be the compensation effect. The rate constant may generally be put in the

Arrhenius form:

$$K = A \exp(-E/RT)$$

It is of interest here to investigate the relationship between the two variables, A and E. In liquid phase reactions in particular, both A and E change in such a way that the corresponding change in the rate is much less than would be the case if only E or A changed alone. This phenomena is known as the compensation effect.

As shown in Figure 17, the two rate constants are equal at 250°K. This temperature is called the isokinetic temperature (Θ) - the temperature at which both rate constants have the same value. Above this temperature, the faster reaction possesses a larger activation energy while below this temperature it has a smaller activation energy. The location of the isokinetic temperature in relation to the experimental temperature range is important. If the isokinetic temperature is in the range of the experimental temperature, the compensation effect may very well be simply a reflection of experimental errors. However, if Θ is far below or above the experimental temperature range and the difference in activation energies is large, there is a definite relationship between K and Θ (see Appendix A). In Figure 19, the washed and oxidized carbon appear to have a

compensating effect. The isokinetic point is not within the experimental range and the two activation energies differ by a factor of about 3.0. However, the isokinetic temperature is -23°C - well below the freezing point of sugar solutions. It is doubtful whether the isokinetic temperature has any real significance at this temperature.

Since the activation energies are low, one might expect they actually represent diffusional activation energies. The temperature dependency of diffusivities can frequently be expressed in terms of an activation energy of diffusion by the familiar expression:

$$D = A_1 \exp(-E/RT)$$

where D is now the effective intraparticle diffusivity in square centimeters per second. It would be expected that the placing of acidic surface oxide groups onto the carbon surface would increase pore diffusional resistance. As shown in Table II the washed unoxidized carbon definitely does have a higher intraparticle diffusional value. All experiments were conducted with moderate agitation eliminating the possibility of interference from bulk diffusion effects in liquid phase.

CONCLUSIONS AND RECOMMENDATIONS

This study has shown that activated carbon "Columbia LC325" reduced the Chemical Oxygen Demand of primary effluent, but only to a small degree. Further work is recommended which could involve the determination of adsorption isotherms with several different types of carbon.

Dextrose, a simple carbohydrate contained in abundance in sewage effluent, adsorbed readily onto the carbon surface. (LC325 and CF300). However, the addition of acidic surface oxide groups measurably reduced the carbons' adsorptive capacity. The higher the concentration of these surface oxides, the slower the rate of adsorption. Removal of the surface oxide groups almost completely restores the carbons' adsorptive capacities. In general, the lower the concentration of acidic surface oxides, the higher is the carbons' adsorptive capacity.

The adsorption capacity of the carbon also depended heavily on the average particle diameter or the total external surface area. Both LC325 and CF300 carbon revealed the same adsorption capacities per gram for equivalent particle diameters.

Activation energies for the CF300 carbon proved to be low, indicating diffusional activation energies. An

explanation for the oxidized carbon sample having a lower activation energy than the washed carbon could not be reached. Again, further work in this area is recommended.

APPENDIX

APPENDIX A

1. Working solutions used in an isotherm run.
2.0, 4.0, 6.0, 8.0, 10.0, 20.0, 30.0, 40.0,
50.0, 60.0 Grams of dextrose / liter

2. Compensation Effect - Relation between K and

$$K = A \text{ EXP}(-E/R \cdot 1/T - 1/\theta) \quad (\text{see Reference 2})$$

K = Reaction rate constant

A = Constant

E = Activation Energy

T = Absolute temperature

θ = Isokinetic temperature

3. Calculation of the Rate Constant K

$$K = (\text{slope}) \times \frac{\text{SVOL}}{\text{GCPSVOL}}$$

$$\frac{\text{g SUGAR}}{\text{ml SOLUTION}} (\text{Hr})^{\frac{1}{2}} \times \frac{\text{ml SOLUTION}}{\text{g CARBON}} = \frac{\text{g SUGAR}}{\text{g CARBON}} (\text{Hr})^{\frac{1}{2}}$$

NOTATION

SVOL	=	Sample Volume, Milliliters
GCPSVOL	=	Grams of carbon per sample volume, grams / liter
EQT	=	Equilibrium time
K	=	Arrhenius reaction rate constant, Moles / gram (hr) ^{1/2}
OSUGC	=	Original sugar concentration, grams / liter
A	=	Arrhenius frequency factor, Moles / gram (hr) ^{1/2}
E	=	Activation energy calories / g-mole
θ	=	Isokinetic temperature, degrees Kelvin
C.O.D.	=	Chemical Oxygen Demand mg. / liter
D	=	Effective intraparticle diffusivity, sq. cm. / sec.
A_1	=	Coefficient in exponential expression for diffusivity, sq. cm. / sec.
T	=	Absolute temperature, degrees Kelvin
T.O.C.	=	Total oxidizable carbon

```

00003 PROGRAM SQUAT(INPUT,OUTPUT,PUNCH)
00003 DIMENSION OSUGC(100),OPTR(100)
00011 READ 5,N
00011 5 FORMAT(I6)
00026 READ 10,(OSUGC(I),OPTR(I),I=1,N)
10 FORMAT(2F20.5)
C OSUGC= ORGINAL SUGAR CONCENTRATION IN GRAMS PER LITER
C OPTR=OPTICAL ROTATION OF SUGAR SOLUTION FROM POLARIMETER
C GCPSVOL= GRAMS OF CARBON PER SAMPLE VOLUME (ML.)
C SVOL= SAMPLE VOLUME USED IN ML)
C SPECRS= SPECIFIC ROTATION OF SUGAR
C WT= MOLECULAR WEIGHT OF SUGAR IN GRAMS PER MOLE
C EQT= EQUILIBRATION TIME IN HOURS
C RSUGC= RESIDUAL SUGAR CONCENTRATION IN GRAMS PER LITER
C RSUGM= RESIDUAL SUGAR CONCENTRATION IN MOLES PER LITER
C XC= GRAMS OF SUGAR PER LITER
C GCPL= GRAMS OF CARBON PER LITER
C X= GRAMS OF SUGAR PER GRAM OF CARBON
C XM= MOLES OF SUGAR PER GRAM OF CARBON
C ADSP= GRAMS OF CARBON PER LITER
00026 GCPSVOL=.5
00027 SVOL=300.0
00031 SPECRS=52.53
00032 WT=360.32
00034 EQT=24.0
00036 PRINT 15,GCPSVOL,SVOL,SPECRS,WT,EQT
00053 15 FORMAT(1H1,////,20X,* GCPSVOL= *,F10.2,/,20X,* SVOL= *,F10.5,
1/,20X,* SPECRS= *,F10.5,/,20X,* WT= *,F10.5,/,20X,* EQT= *,F10.5
PRINT 16
00053 16 FORMAT(/,20X,*SUGAR = LACTOSE*,/,20X,*CARBON TYPE = LC325*)
00057 PRINT 11
00057 11 FORMAT(/,10X,*OSUGC*,10X,*OPTR*,11X,*RSUGC*,10X,*RSUGM*,13X,*XC
1,12X,*X*,13X,*XM*,12X,*ADSP*,/,10X,*G/L*,12X,*DEG*,
212X,*G/L*,11X,*MOLE/L*,12X,*G/L*,10X,*GS/GC*,10X,*MS/GC*,
311X,*GC/L*)
00063 DO 101 I=1,N
00065 RSUGC=(1000.0*OPTR(I))/(2.0*SPECRS)
00070 RSUGM=RSUGC/WT
00072 XC=OSUGC(I)-RSUGC
00075 GCPL=(GCPSVOL/SVOL)*1000.0
00077 X=XC/GCPL
00101 XM=X/WT
00103 ADSP=RSUGM/XM
00105 PRINT 100,OSUGC(I),OPTR(I),RSUGC,RSUGM,XC,X,XM,ADSP
00130 100 FORMAT(/,8F15.5)
00130 PUNCH 200,RSUGC,X
00140 200 FORMAT(2F20.5)
00140 101 CONTINUE
00143 CALL EXIT
00144 END

```

TABLE I

RESULTS OF C. O. D. ADSORPTION TESTS

WASTE	CARBON SIZE	CARBON CONC.	C.O.D.		% REDUCTION
			START	FINAL	
			mg/l		
SECONDARY EFFLUENT*	ACTIVATED	0.25g/l	52.0	45.0	13.5
	LC325				
	COLUMBIA	0.25g/l	52.0	43.8	15.75
		0.25g/l	52.0	44.8	13.85
		0.25g/l	52.0	40.5	22.10

* Sewage was obtained from the Bethlehem trickle-filter plant. (Bethlehem, Pennsylvania)

TABLE II.

SUMMARY OF KINETIC RESULTS

CARBON SAMPLE	(NH ₄) ₂ S ₂ O ₈ MOLAR CONC. 3 - DAYS EQT.	PARTICLE SIZE* RANGE IN MM.	K MICROMOLES/ GRAM (Hr) ^{1/2}	TEMPERATURE °C	TOTAL ACIDITY MEQ/GRAM
CF300-W	0.0	2.38 - 2.83	666	19.0	.70
CF300-W	0.0	1.41 - 1.68	1166	19.0	
CF300-W	0.0	0.595 - 0.707	1600	19.0	
CF300-W	0.0	2.38 - 2.83	867	40.0	.70
CF300-W	0.0	2.38 - 2.83	666	19.0	.70
CF300-W	0.0	2.38 - 2.83	520	0.0	.70
CF300-O	0.4	2.38 - 2.83	476	40.0	3.50
CF300-O	0.4	2.38 - 2.83	432	19.0	3.50
CF300-O	0.4	2.38 - 2.83	394	0.0	3.50
CF300-O	0.8	2.38 - 2.83	312	19.0	3.50

* All particles were sieved after oxidation.

TABLE III

SURFACE AREAS FROM LANGMUIR PLOTS

SAMPLES	SLOPE g/mole	V_m MILLIMOLE/g	SURFACE AREA* M^2/g	B.E.T. SURFACE AREA M^2/g	PERCENT OF SURFACE OCCUPIED BY DEXTROSE
LC325 - W	820	1.22	365	1076	34
LC325 - OR	850	1.18	354	840	42
LC325 - O	1850	0.54	162	861	19
CF300 - W ¹	1100	0.90	270	950	29

* Computed from V_m and crosssectional area of dextrose molecule.

¹ Particle size range 1.41 - 1.63 mm.

TABLE IV

SURFACE ACIDITIES AND SURFACE AREAS OF CARBON SAMPLES

	BASE CONSUMPTION(MEQ./GRAM)				TOTAL ACIDITY MEQ/GRAM	B.E.T.(N ₂) M ² /G
	NaOEt	NaOH	Na ₂ CO ₃	NaHCO ₃		
LC325 W	.59	.48	.28	.30	.59	1076
LC325 O	3.10	2.92	2.05	1.50	3.10	861
LC325 OR	2.46	2.10	1.29	.92	2.46	840
CF300 W ¹	.70				.70	950
CF300 O ¹	3.50				3.50	

Note: W - Washed Carbon, O - Oxidized Carbon, OR - Oxidized Reduced Carbon.

¹
Particle Size Range 2.38 - 2.83 mm

TABLE V

RATE EXPRESSIONS

CF300 Washed Carbon
Particle Size Range 2.38 - 2.83 mm

$$K = 34.5 \times 10^{-3} \text{ EXP } (-2290/RT)$$

$$\text{Frequency Factor} = 34.5 \times 10^{-3} \text{ Micro Moles/Gram (Hr)}^{\frac{1}{2}}$$

$$\text{Activation Energy} = 2290 \text{ Calories/ Mole}$$

$$K = 666 \text{ Micro Moles/Gram (Hr)}^{\frac{1}{2}} \text{ at } 19.0^{\circ}\text{C}$$

CF300 Oxidized Carbon
Particle Size Range 2.38 - 2.83 mm

$$K = 1.7 \times 10^{-3} \text{ EXP } (-785/RT)$$

$$\text{Frequency Factor} = 1.7 \times 10^{-3} \text{ Micro Moles/Gram (Hr)}^{\frac{1}{2}}$$

$$\text{Activation Energy} = 785 \text{ Calories/ Mole}$$

$$K = 432 \text{ Micro Moles/ Gram (Hr)}^{\frac{1}{2}} \text{ at } 19.0^{\circ}\text{C}$$

Comparisons

Frequency Factors

$$A \text{ (washed)} = 20.3XA \text{ (oxidized)}$$

Activation Energies

$$E \text{ (washed)} = 2.92XE \text{ (oxidized)}$$

TABLE VI

SURFACE ACIDITIES AND SURFACE AREAS OF CARBON ADSORBENT SAMPLES

SAMPLE DESIGNATION	CARBON TYPE	PARTICLE SIZE RANGE MM.	CARBON TREATMENT	TOTAL ACIDITY MEQ/GRAM	B.E.T. SURFACE AREA (N ₂) M ² /g
LC325 - W	COLUMBIA ACTIVATED CARBON LC325	ACTIVATED*	WASHED	0.59	1076
LC325 - O		ACTIVATED*	OXIDIZED	3.10	861
LC325 - OR		ACTIVATED*	OXIDIZED-REDUCED	2.46	840
CF300 - W	GALGON FILTRASORB CARBON CF300	2.38 - 2.83	WASHED	0.70	950
CF300 - O		2.38 - 2.83	OXIDIZED	3.50	

* Passes through U. S. Standard sieve No. 325, sieve opening 0.044 mm.

TABLE VII

SUMMARY OF INFORMATION ON CARBON SAMPLES

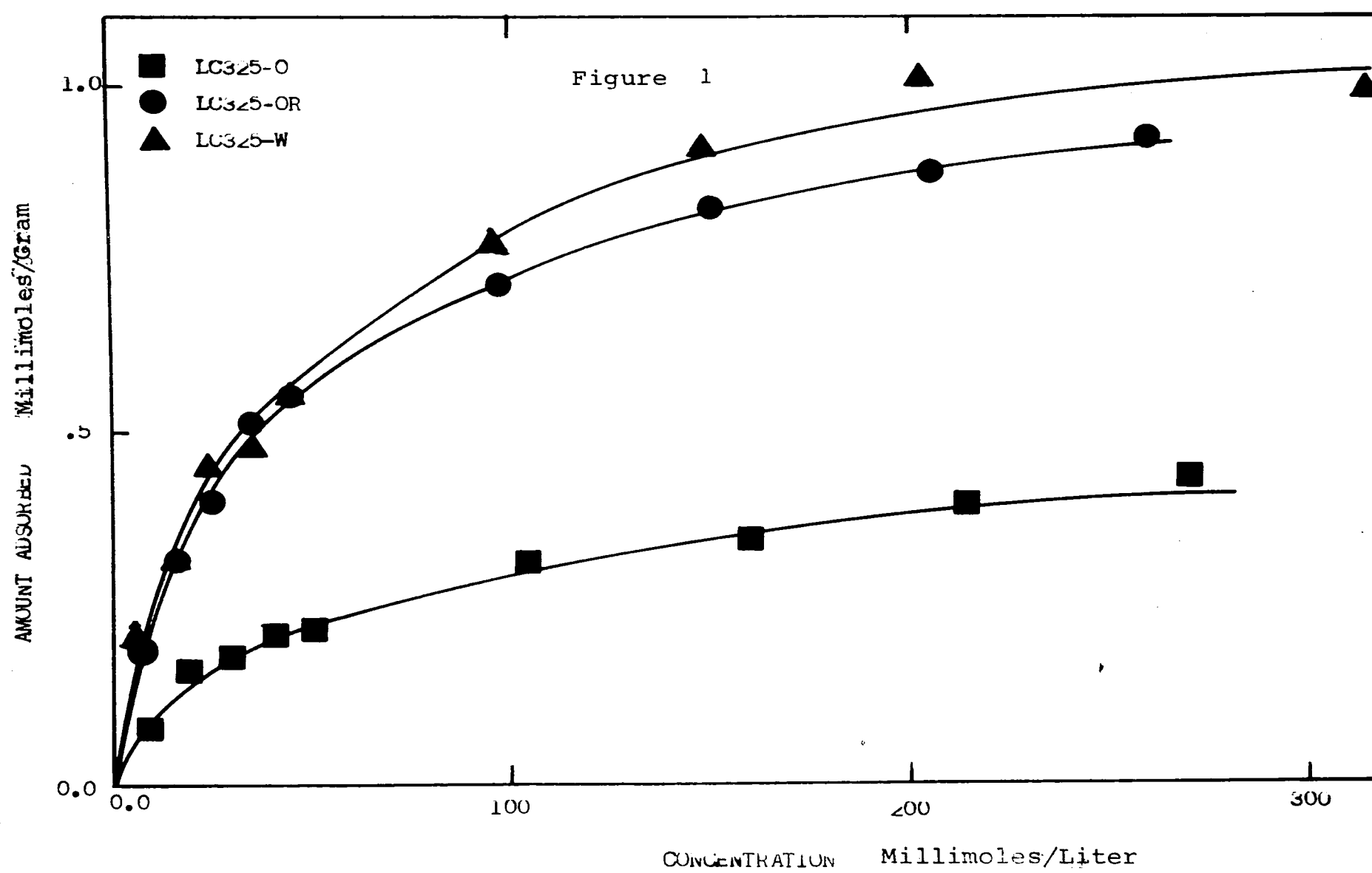
PHYSICAL PROPERTIES AND SPECIFICATIONS	COLUMBIA ACTIVATED CARBON LC325 UNION CARBIDE CORP.	CALGON FILTRASORB CARBON CF300 (SGL) CALGON CORP.
Total Surface Area (N ₂ , B.E.T. Method) M ² /g	1076	950
Apparent Density g/cc	0.5	0.48
Moisture (percent)	1.0	2.0
Ash Content (percent residue after ignition)	2.0	8.0
Iodine Number (minimum)	--	900
Molasses Number (minimum)	--	200
Particle Size Range mm	- 0.044	3.36 - 0.044

TABLE VIII

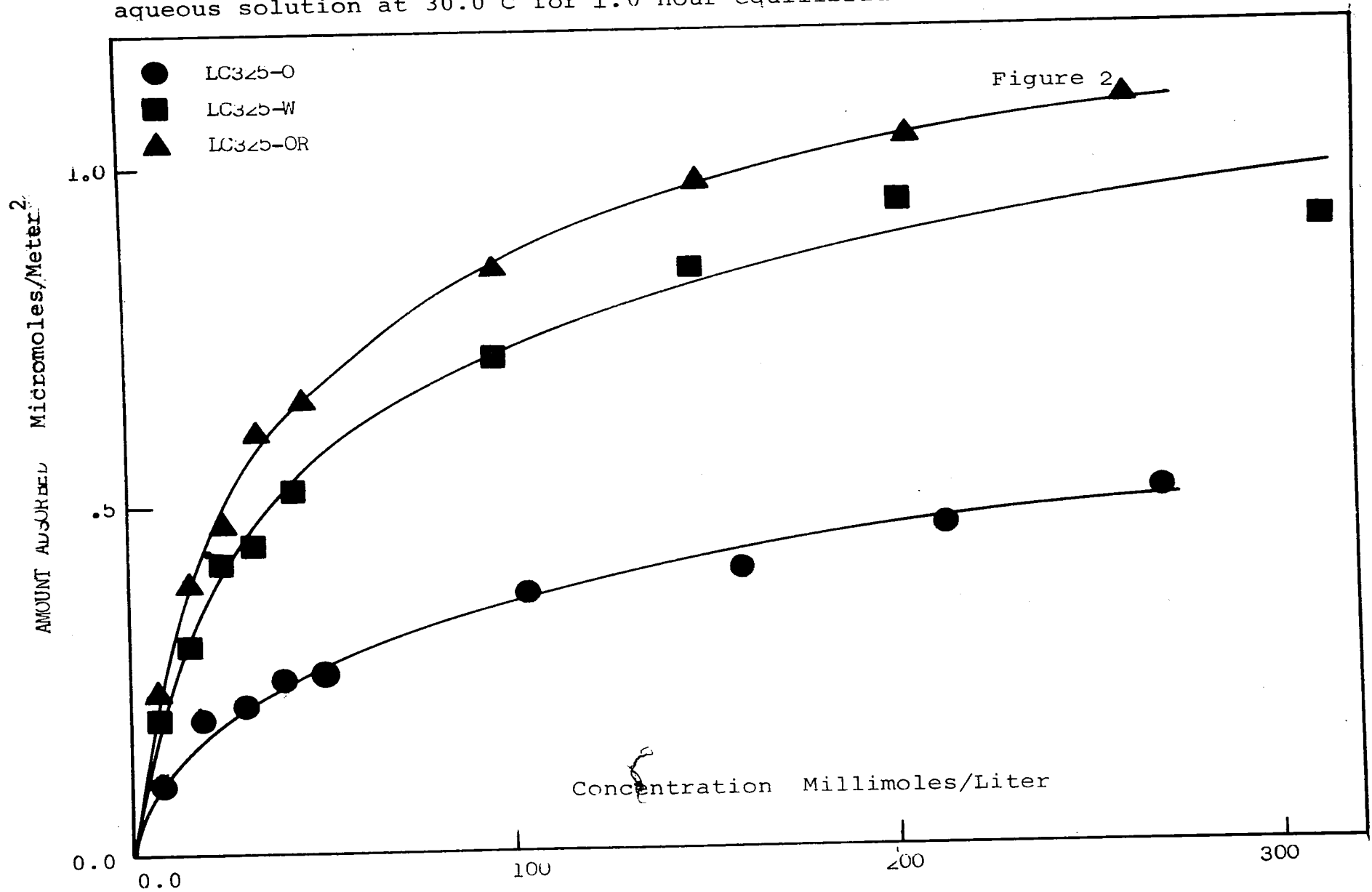
SPECIFICATIONS FOR U. S. STANDARD SIEVE SIZES USED

<u>SIEVE NUMBER</u>	<u>SIEVE OPENING MM</u>
6	3.36
7	2.83
8	2.38
12	1.68
14	1.41
18	1.00
25	0.207
30	0.595
50	0.297
60	0.250
230	0.063
270	0.053

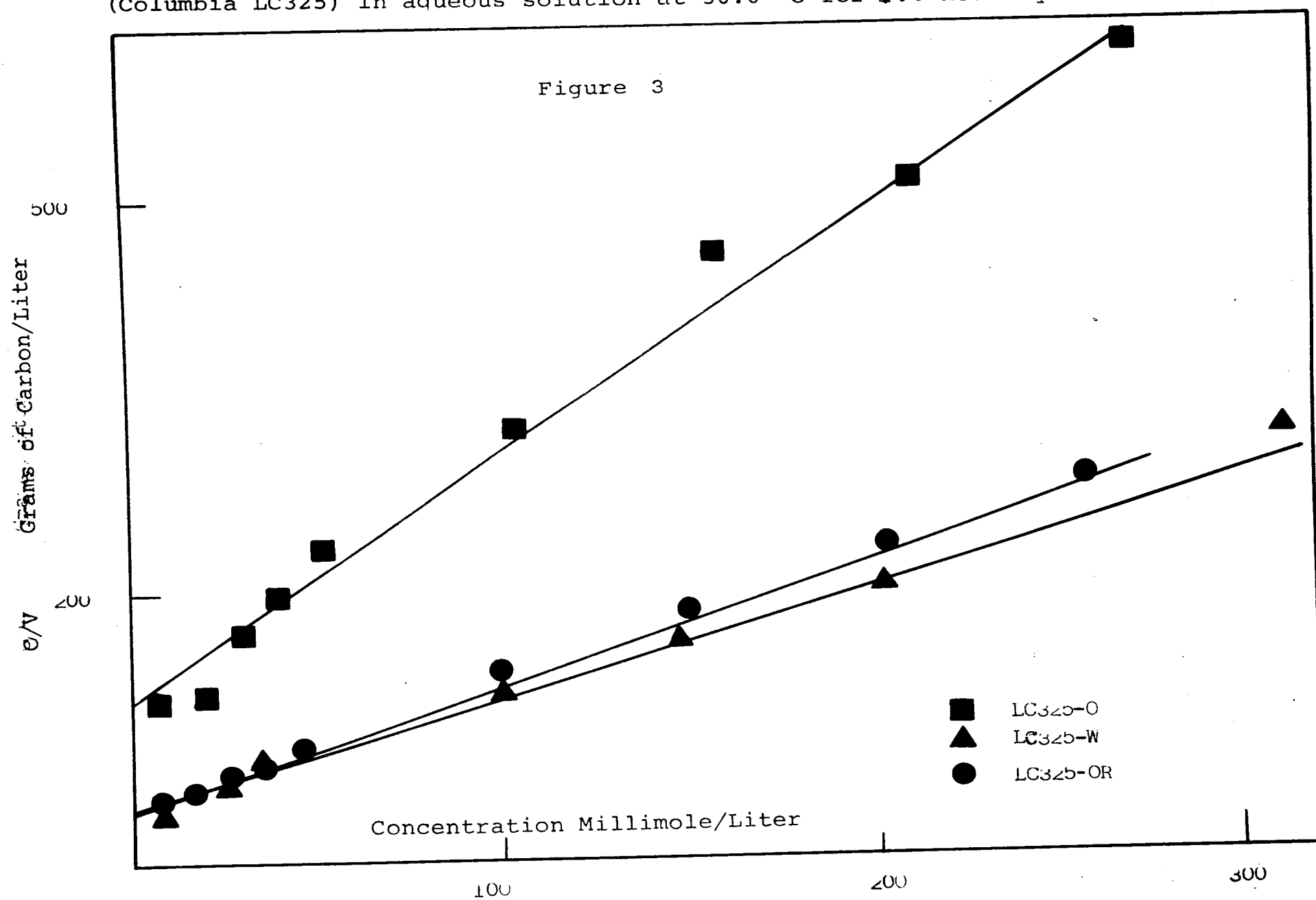
Adsorption Isotherms of Dextrose on activated carbon (Columbia Lc325) in aqueous solution at 30.0 °C for 1.0 hour equilibrium time on a per gram basis.



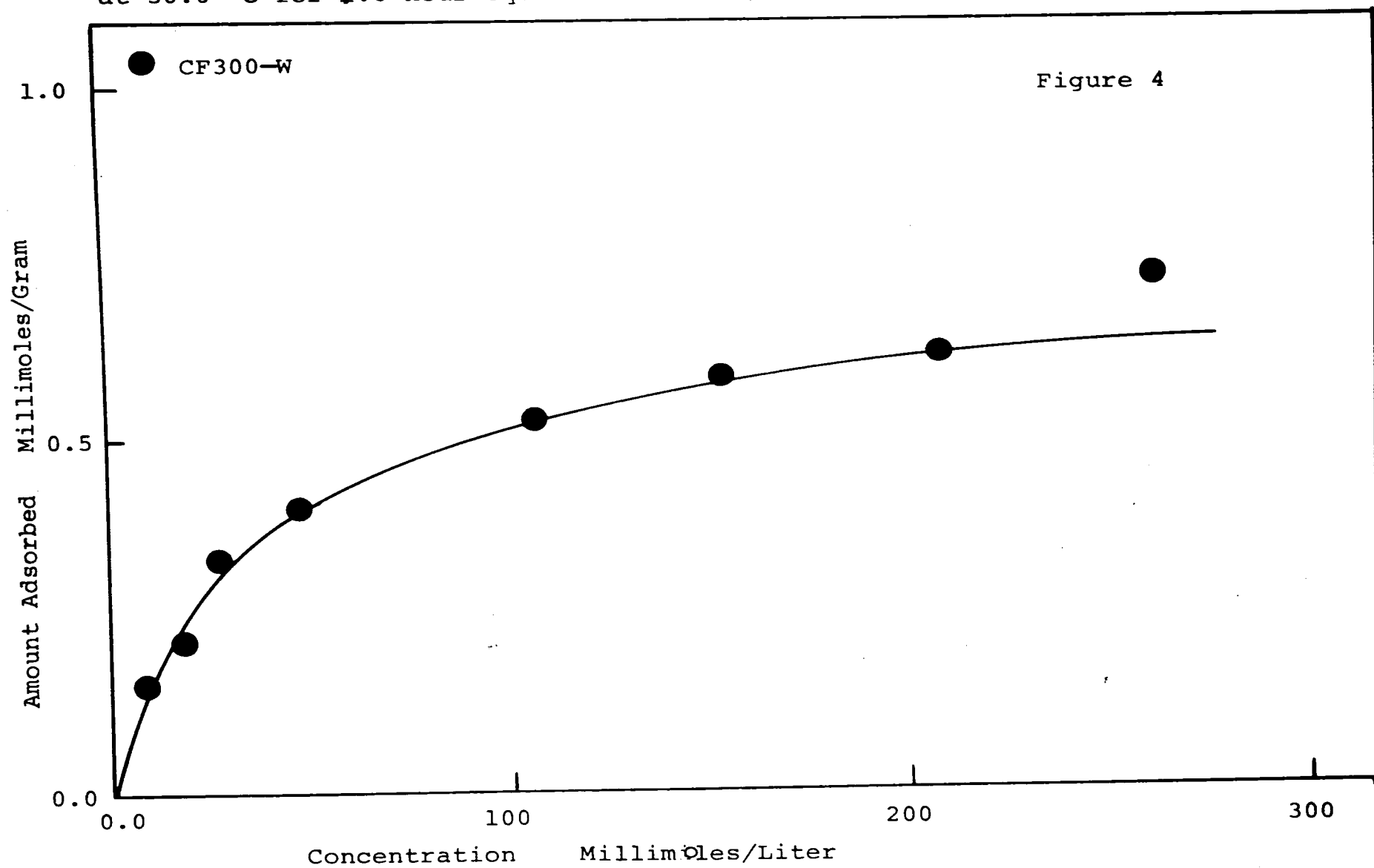
Adsorption Isotherms of Dextrose on activated carbon (Columbia LC325) in aqueous solution at 30.0°C for 1.0 hour equilibrium time. (Per unit BET surface area basis)



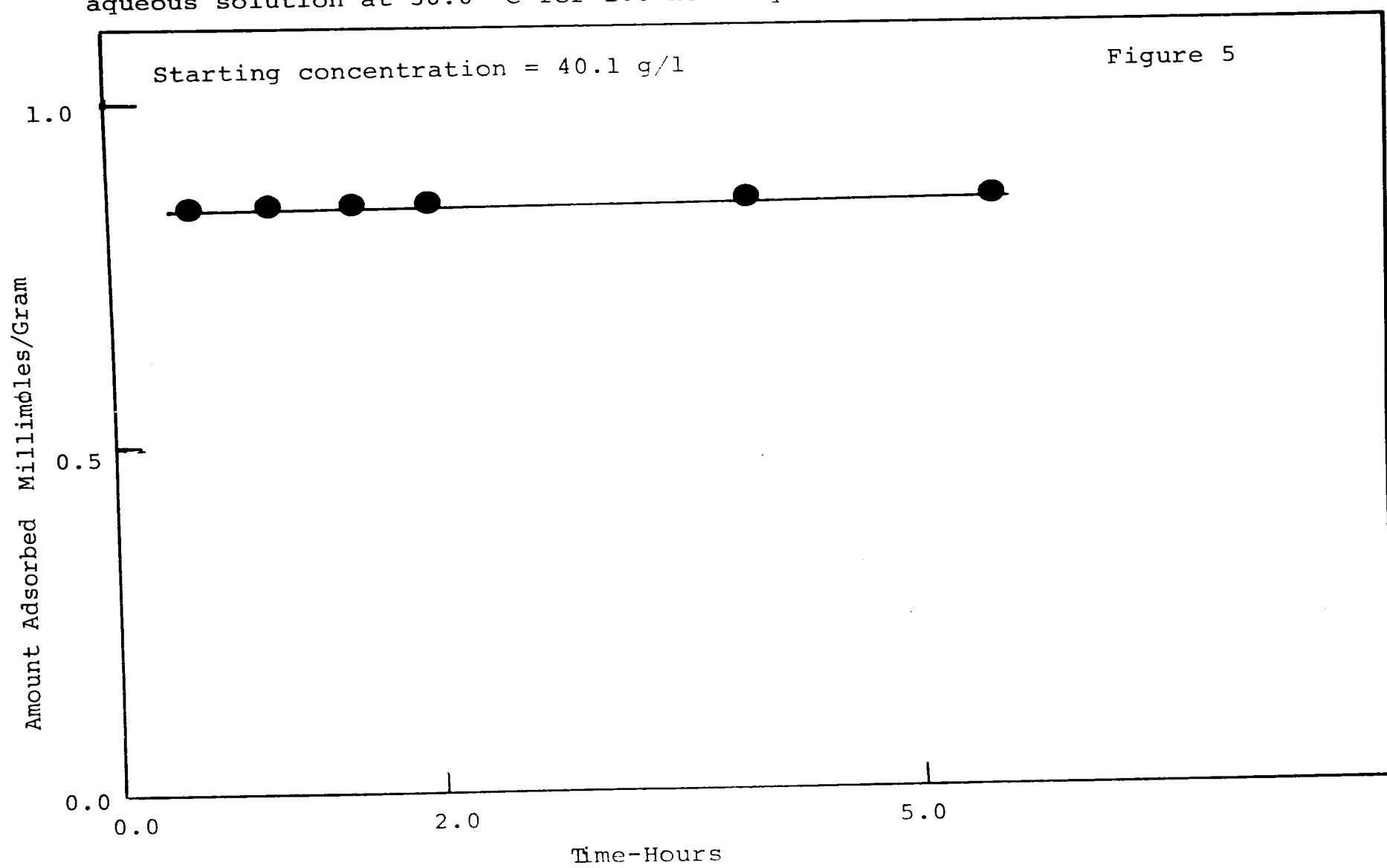
Langmuir Plots of adsorption isotherms for Dextrose on activated carbon (Columbia LC325) in aqueous solution at 30.0 °C for 1.0 hour equilibrium time



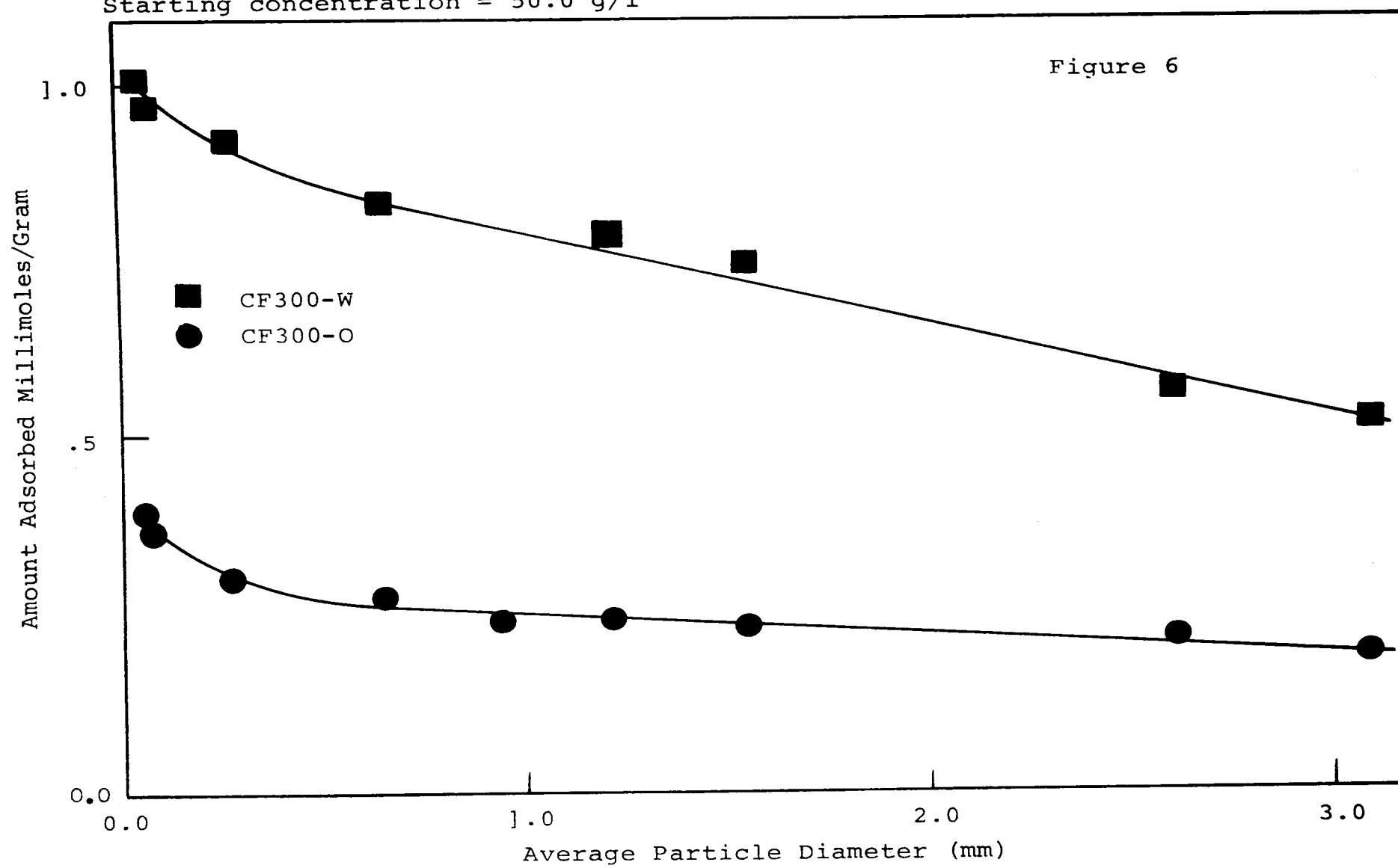
Adsorption Isotherm of Dextrose on CF300-W Carbon in aqueous solution
at 30.0 °C for 1.0 hour equilibrium time, Particle size range 1.41-1.68 mm.

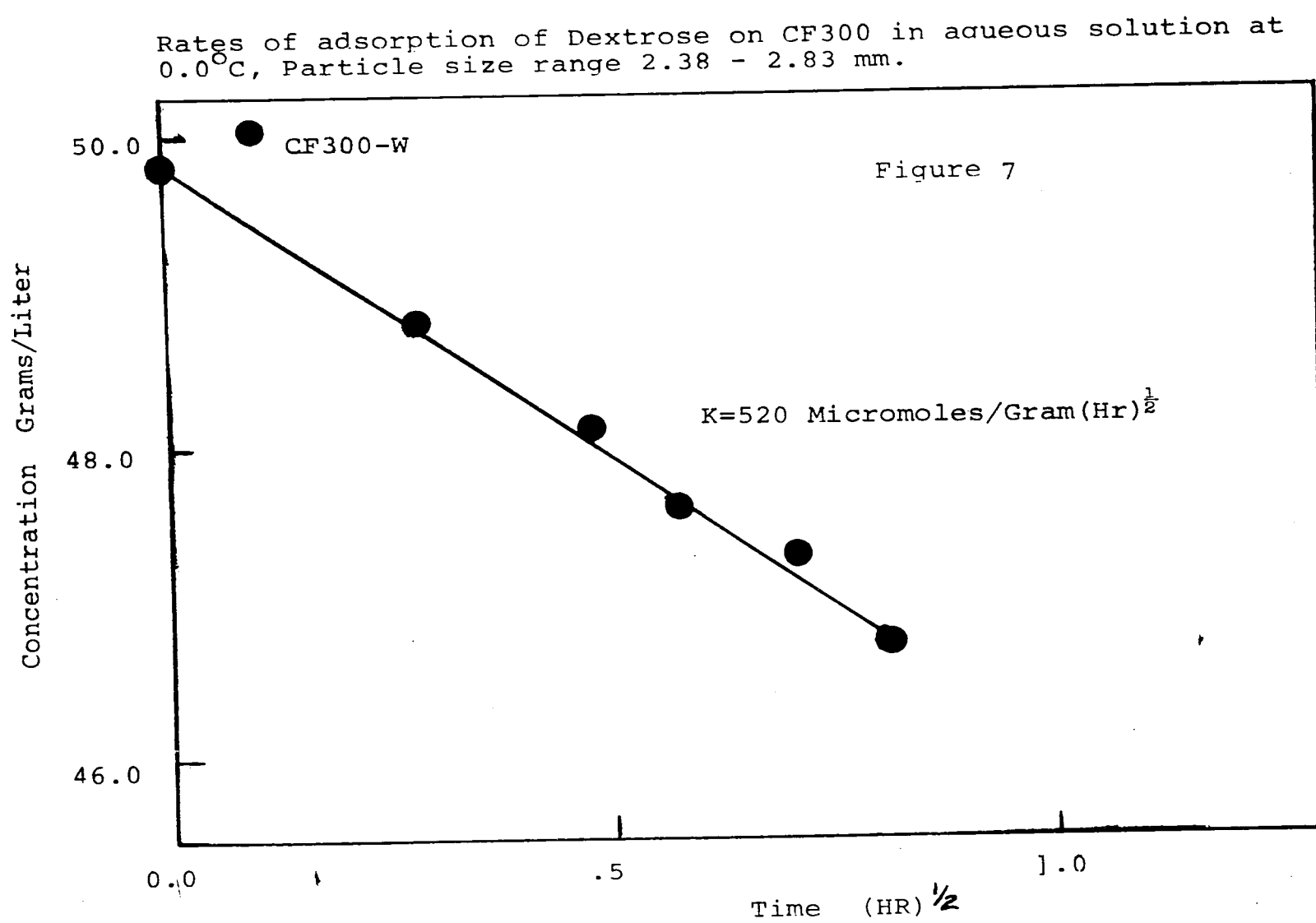


Rates of adsorption of Dextrose on activate carbon (Columbia LC325) in aqueous solution at 30.0 °C for 1.0 hour equilibrium time..

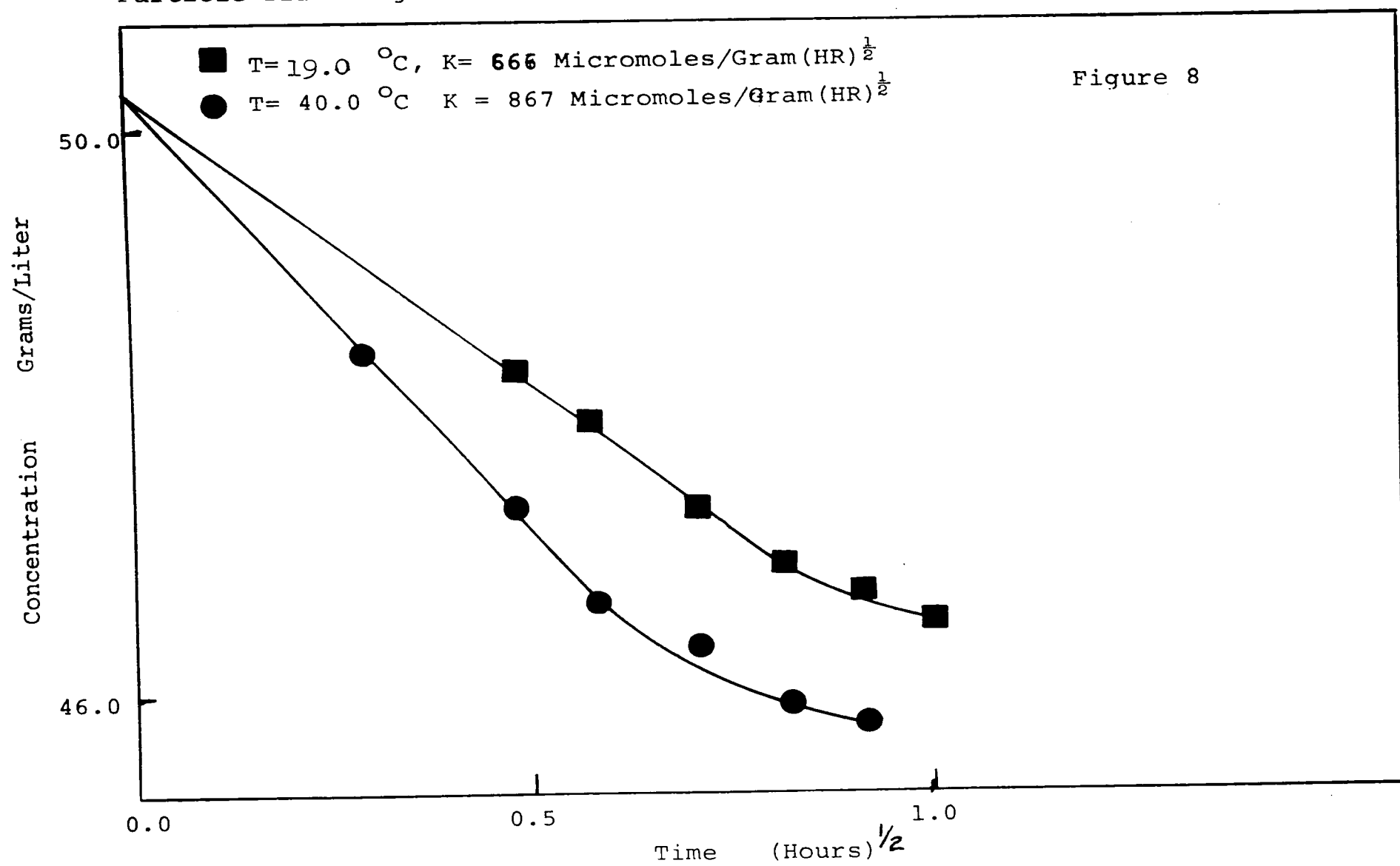


Effect of particle size on the adsorption of Dextrose on CF300 in aqueous solution at 30.0°C for 1.0 hour equilibrium time.
Starting concentration = 50.0 g/l

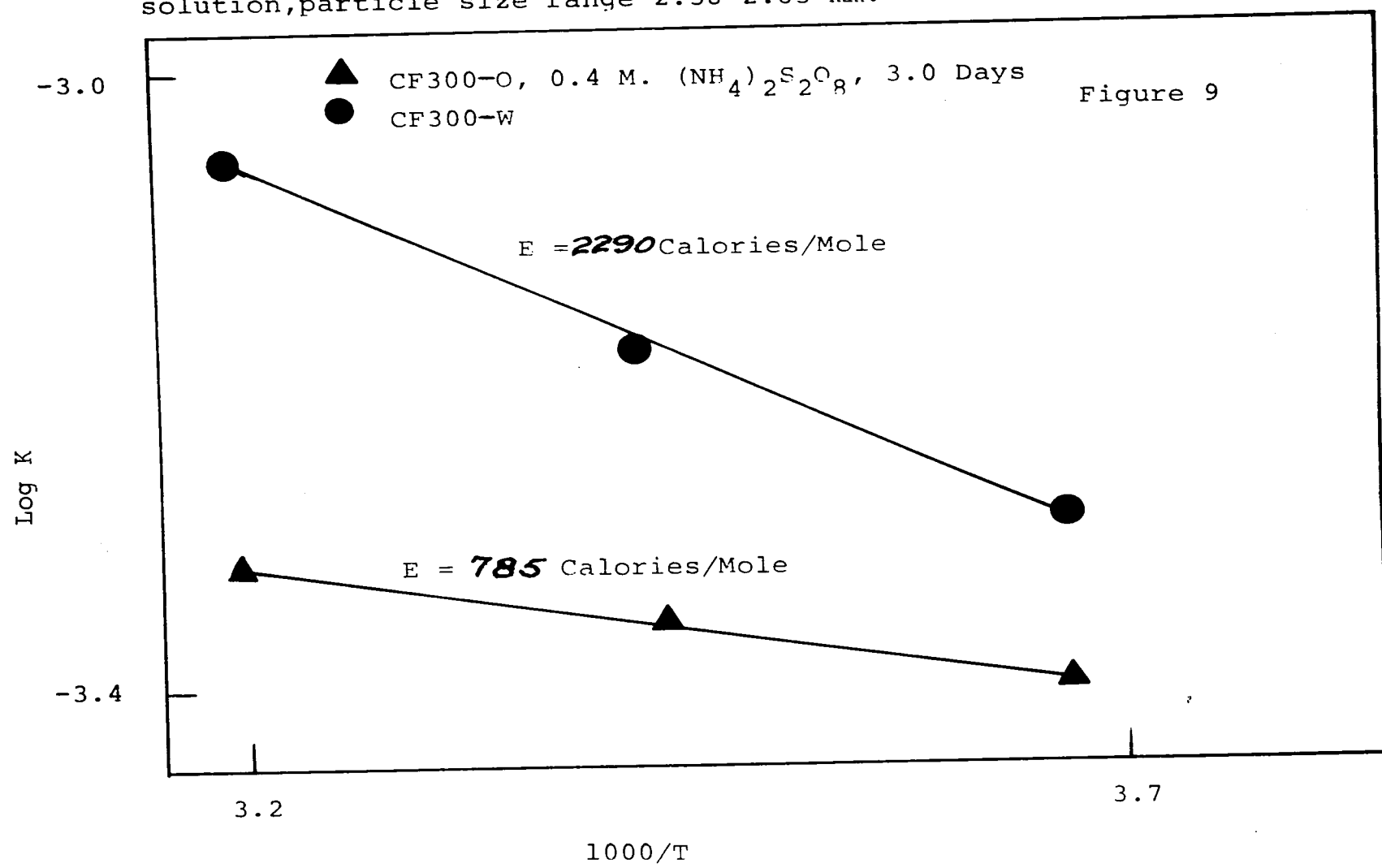




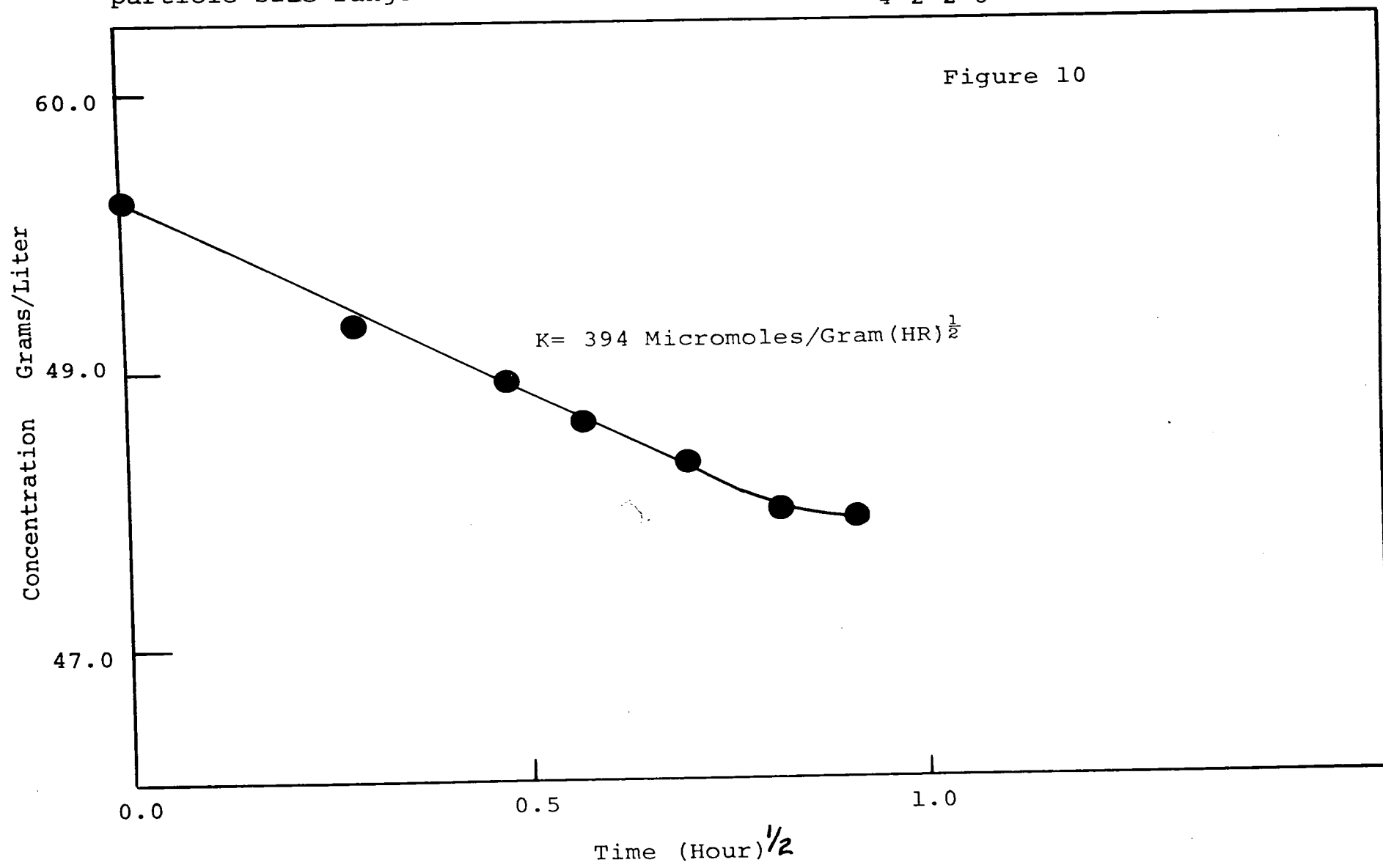
Rates of adsorption of Dextrose on CF300 W in aqueous solution,
Particle size range 2.38-2.83 mm.



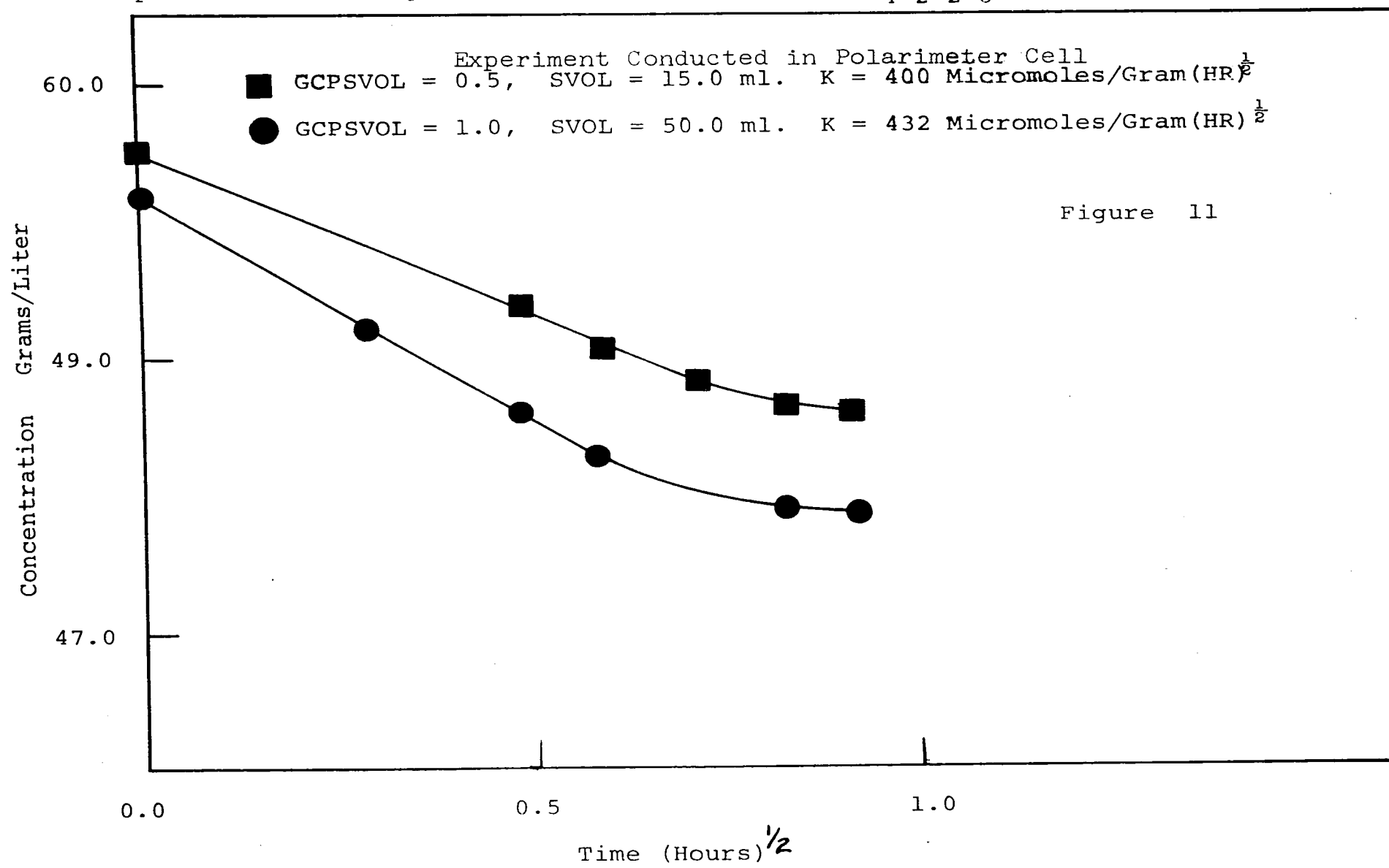
Log K versus $1000/T$ for the adsorption of Dextrose on CF300 in aqueous solution, particle size range 2.38-2.83 mm.



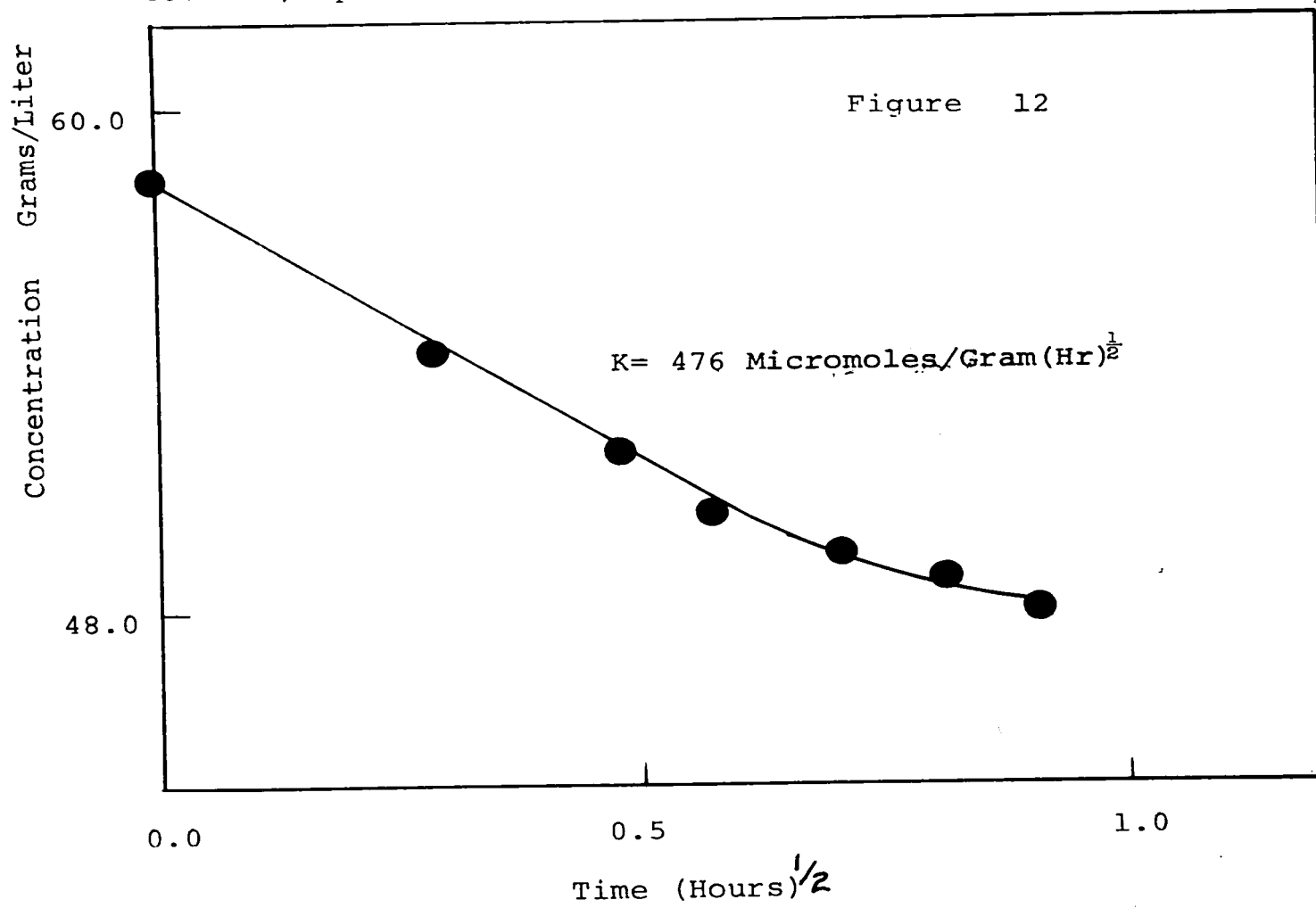
Rates of adsorption of Dextrose on CF300-O in aqueous solution at 0.0 °C
particle size range 2.38-2.83 mm., 0.4 Molar $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - 3.0 Days.



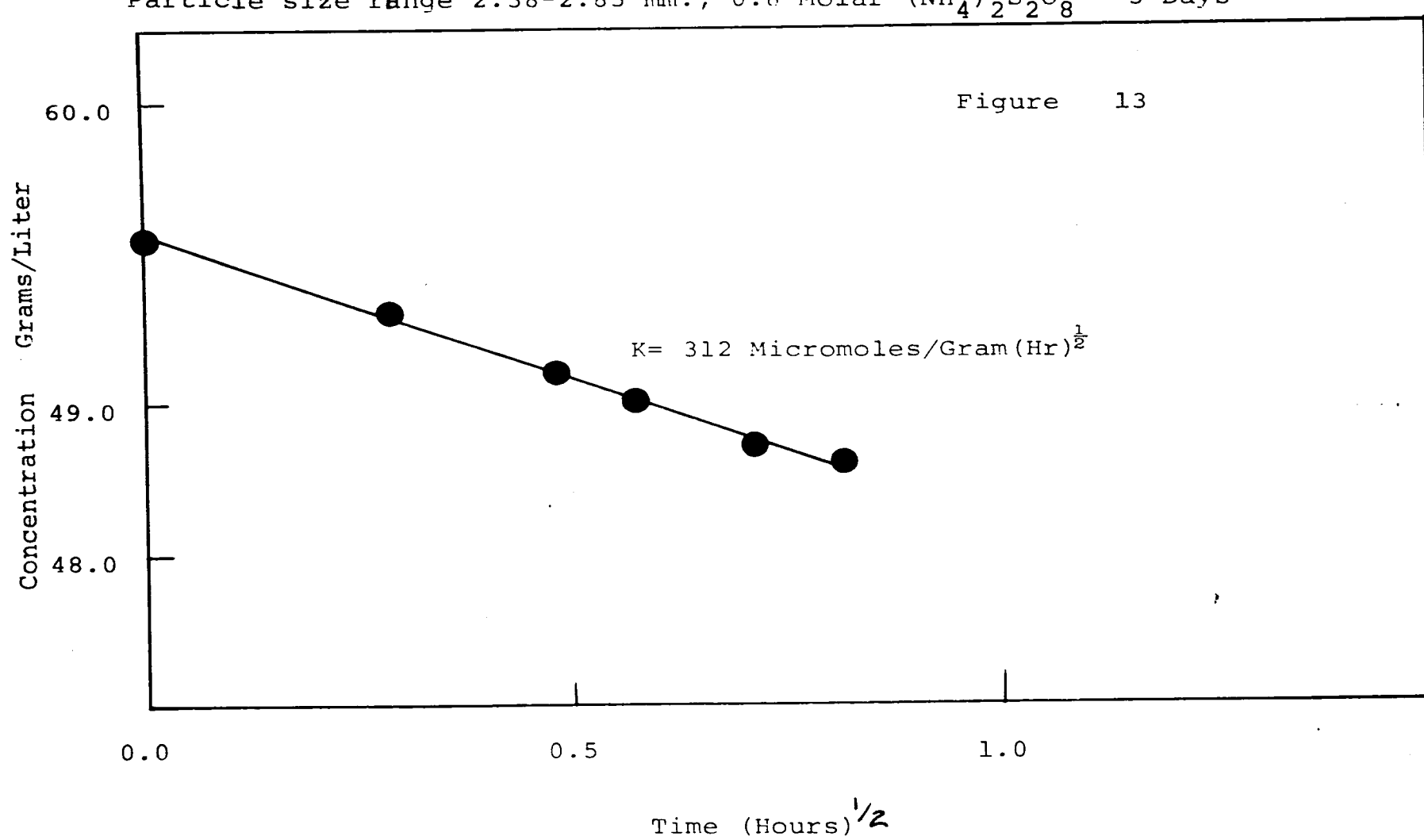
Rates of adsorption of Dextrose on CF300-O in aqueous solution at 17.0 °C,
particle size range 2.38-2.83 mm, 0.4 Molar $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - 3 Days



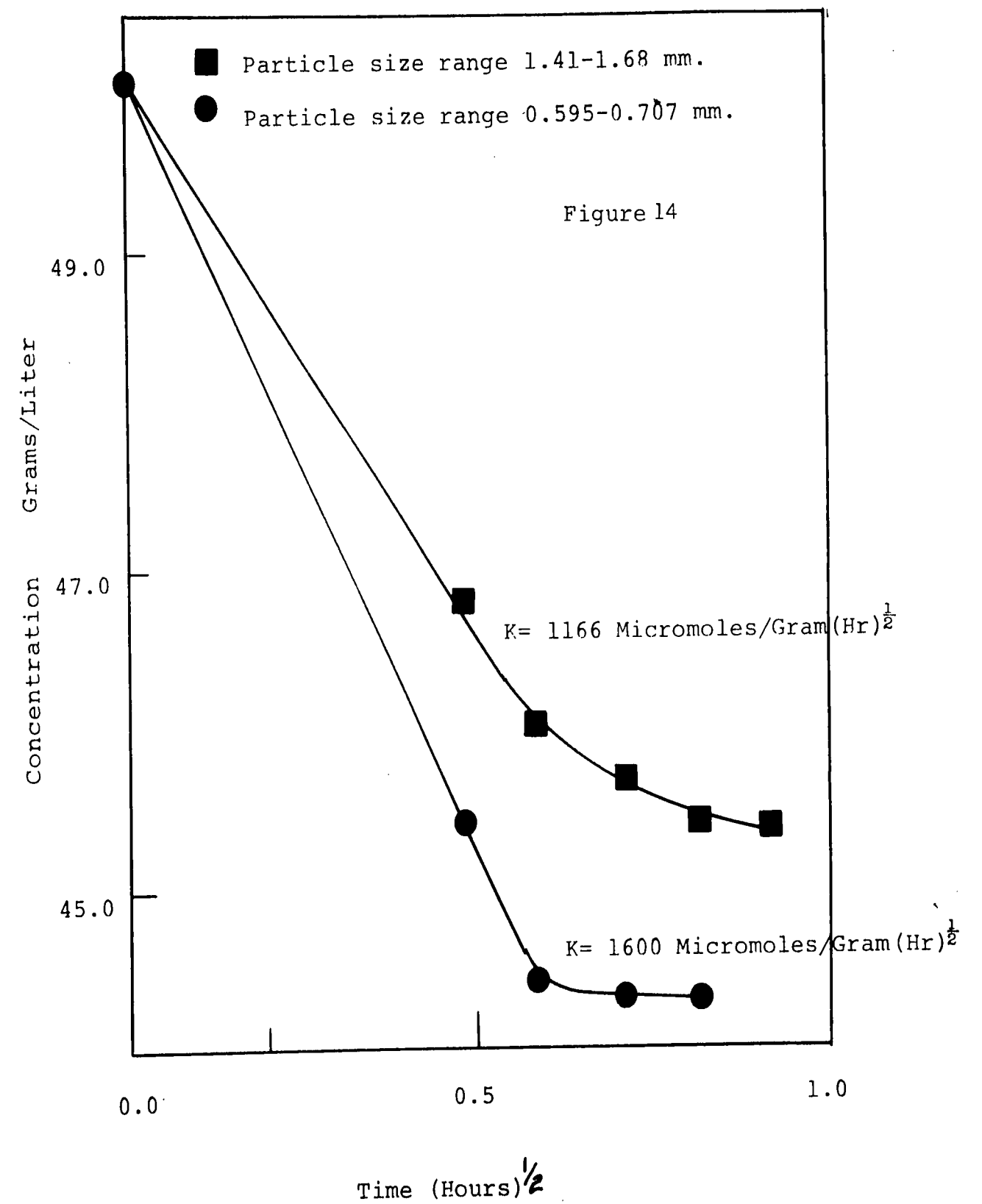
Rate of adsorption of Dextrose on CF300-O in aqueous solution at
40.0 °C, particle size range 2.38 - 2.83 mm., $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - 0.4 Molar



Rate of adsorption of Dextrose on CF300-O carbon in aqueous solution at 19.0 °C
Particle size range 2.38-2.83 mm., 0.8 Molar $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - 3 Days



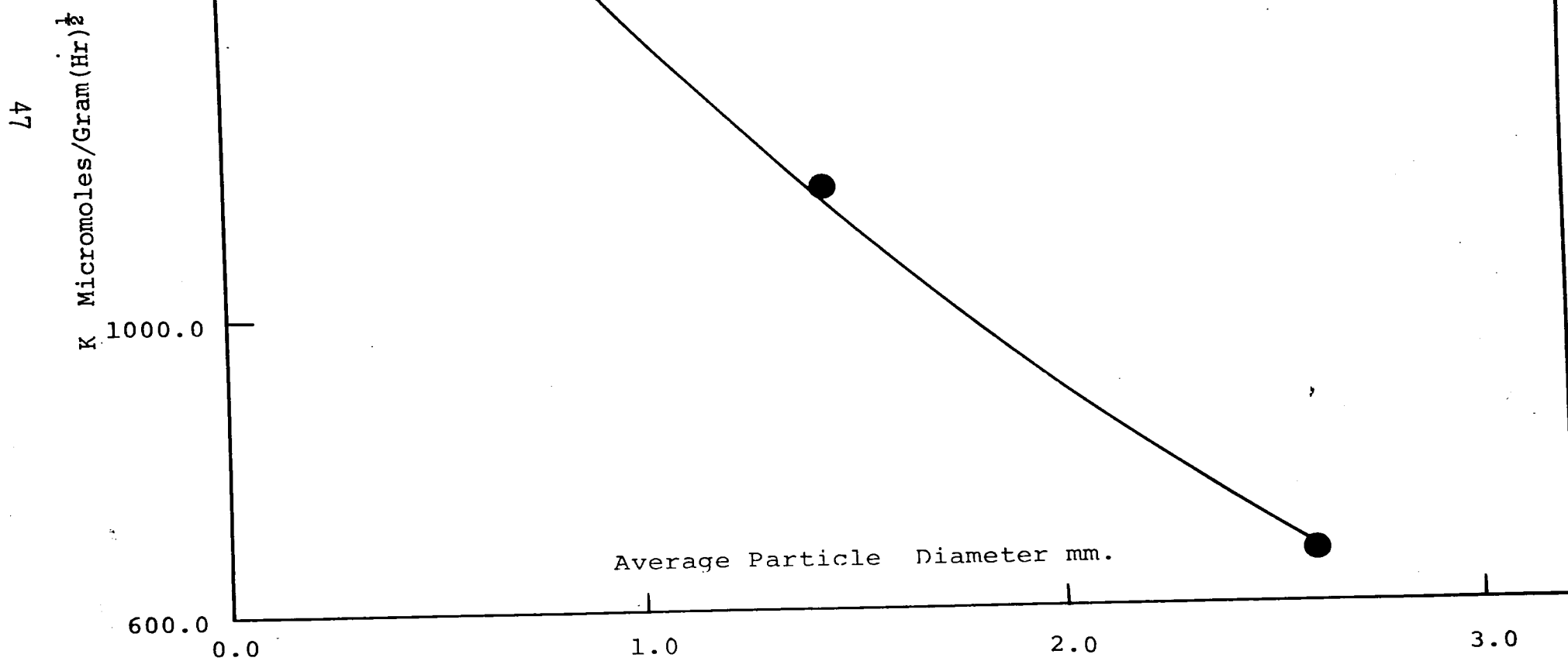
Rate of adsorption of Dextrose on CF300 washed carbon in aqueous solution at 19.0 °C



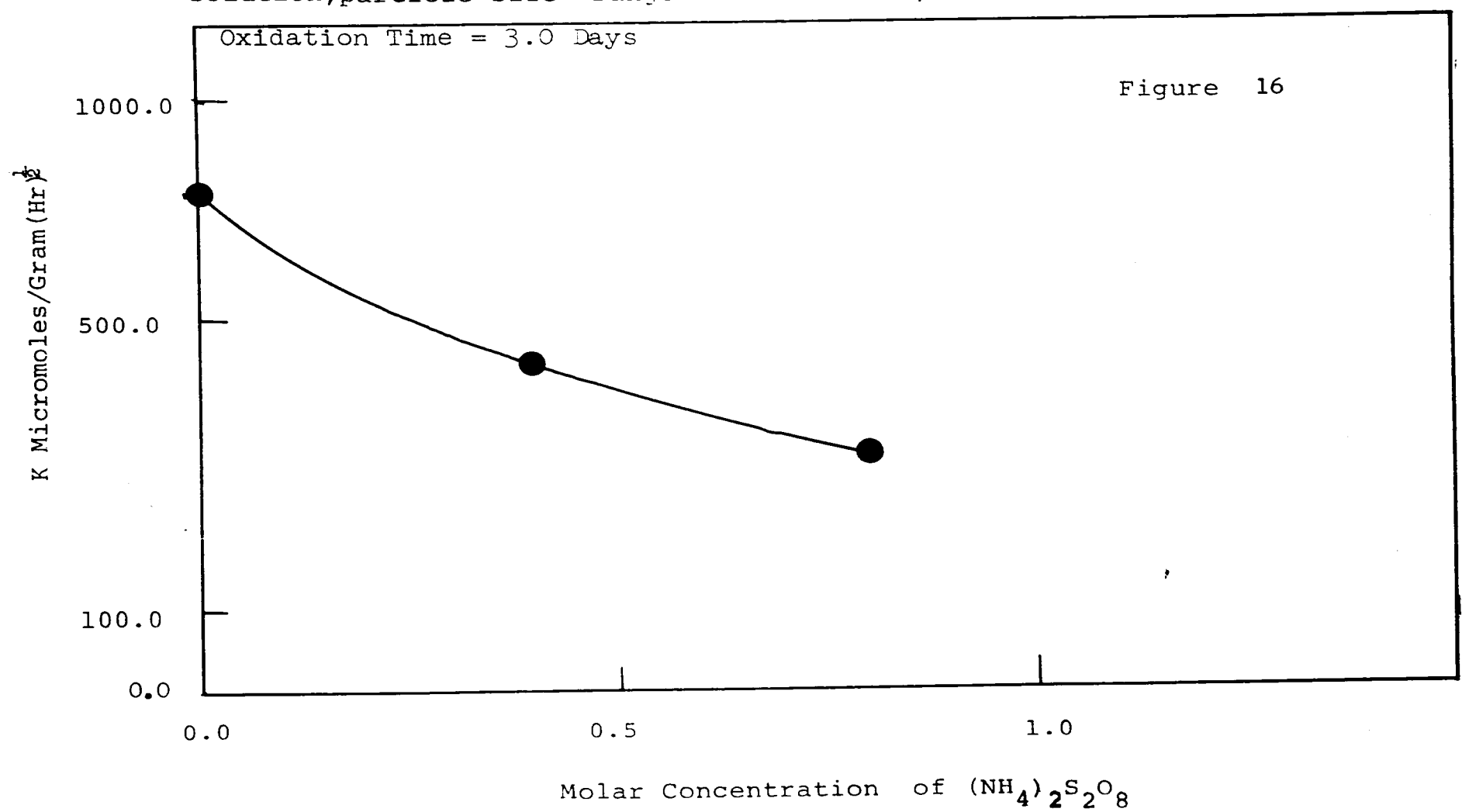
Effect of particle size on the rate constant K in aqueous solution at 19.0 °C

CF300 washed carbon

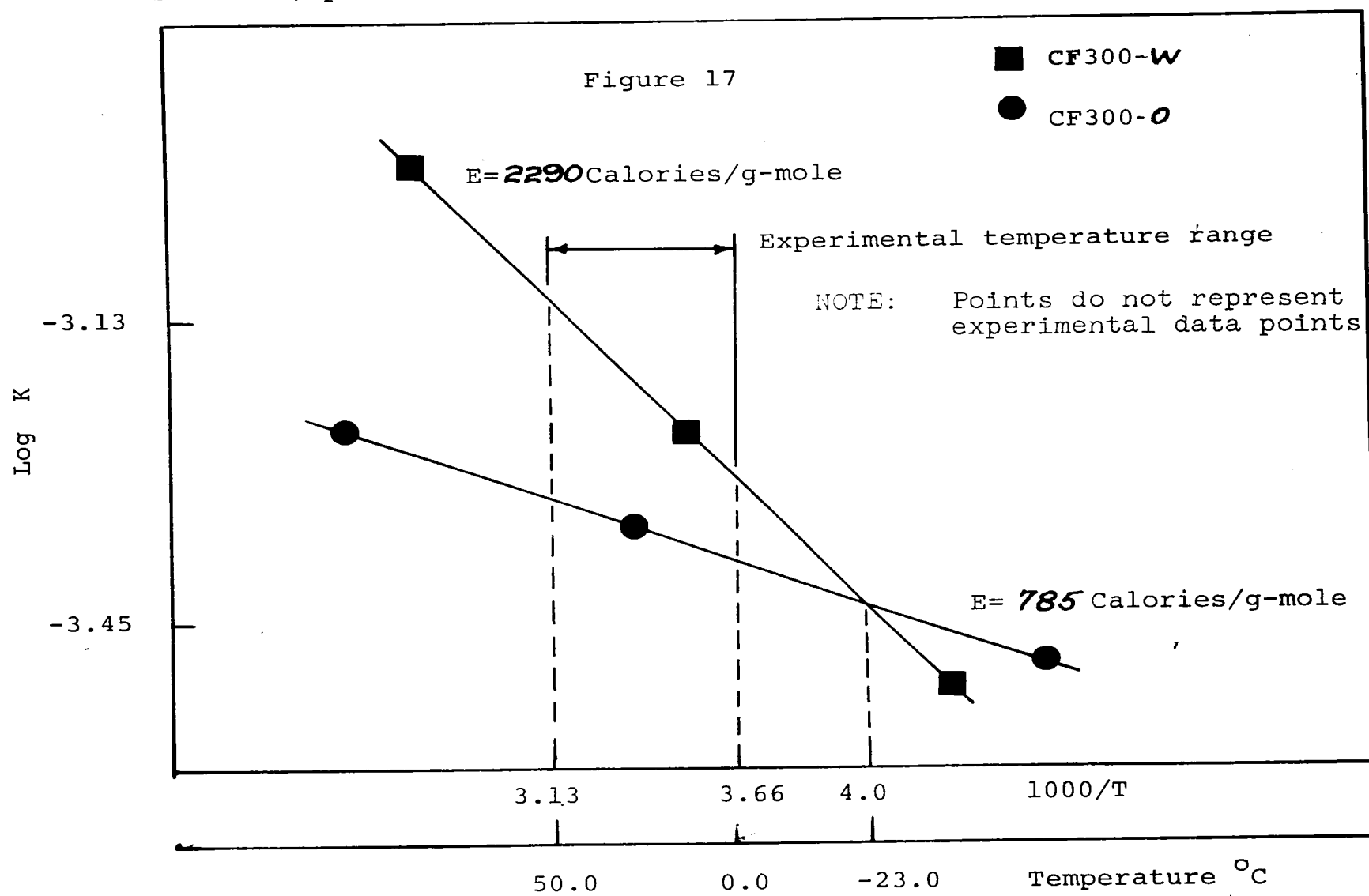
Figure 15



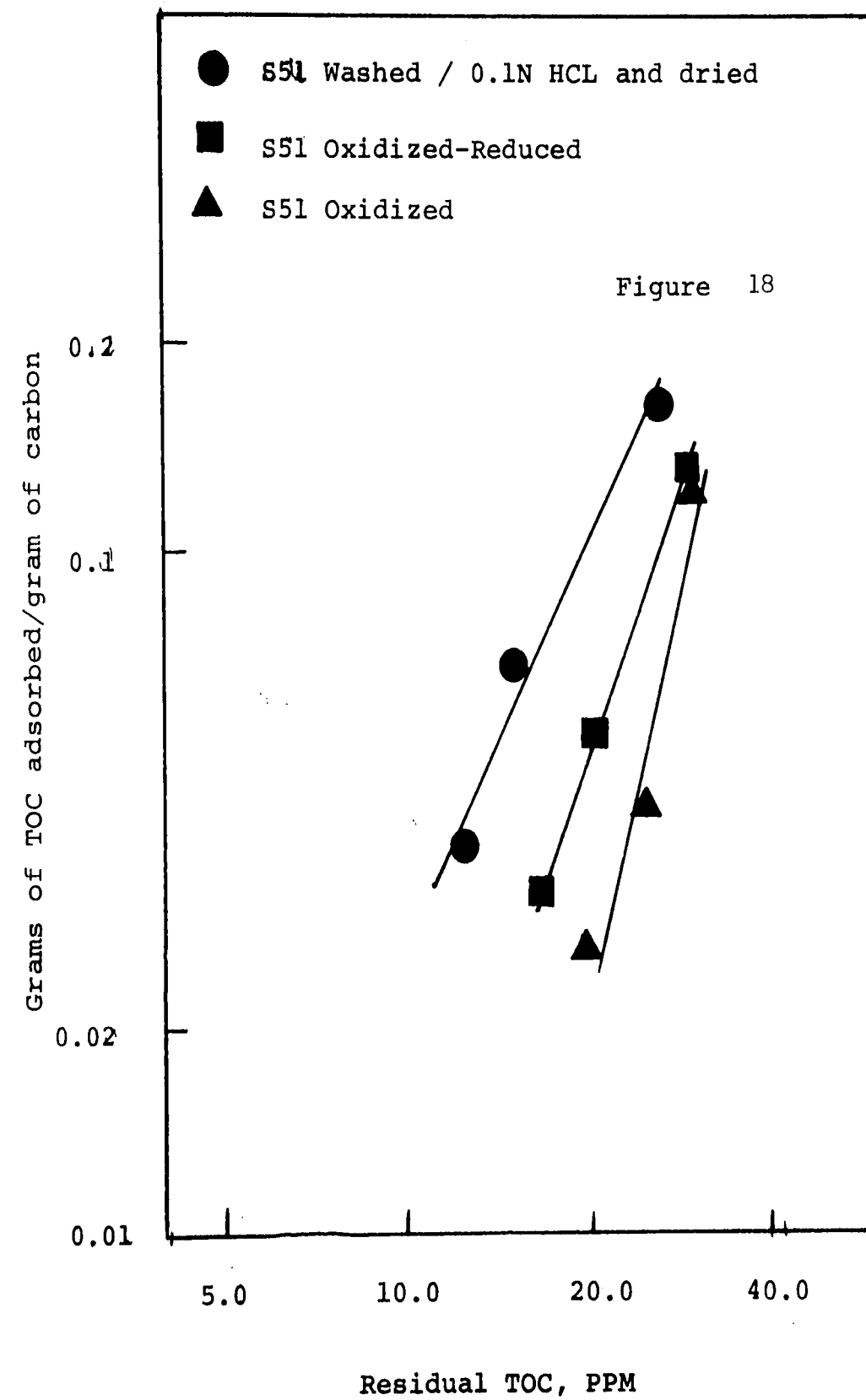
Effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ Concentration on the rate constant K in aqueous solution, particle size range 2.38-2.83 mm., at 19.0 °C CF300 Carbon



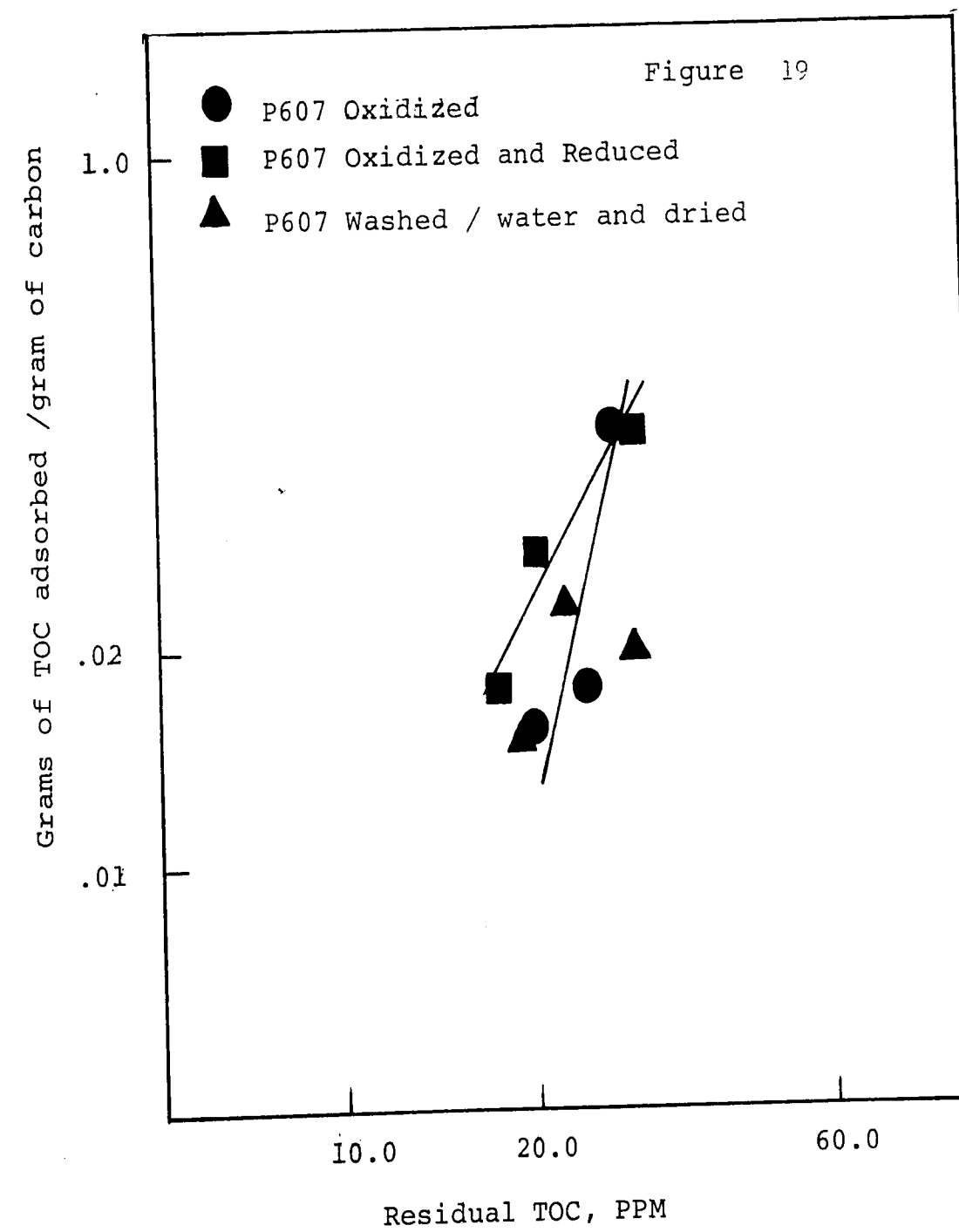
Log K versus $1.0/T$ for the adsorption of Dextrose on CF300 in aqueous solution, particle size range 2.38-2.83mm.



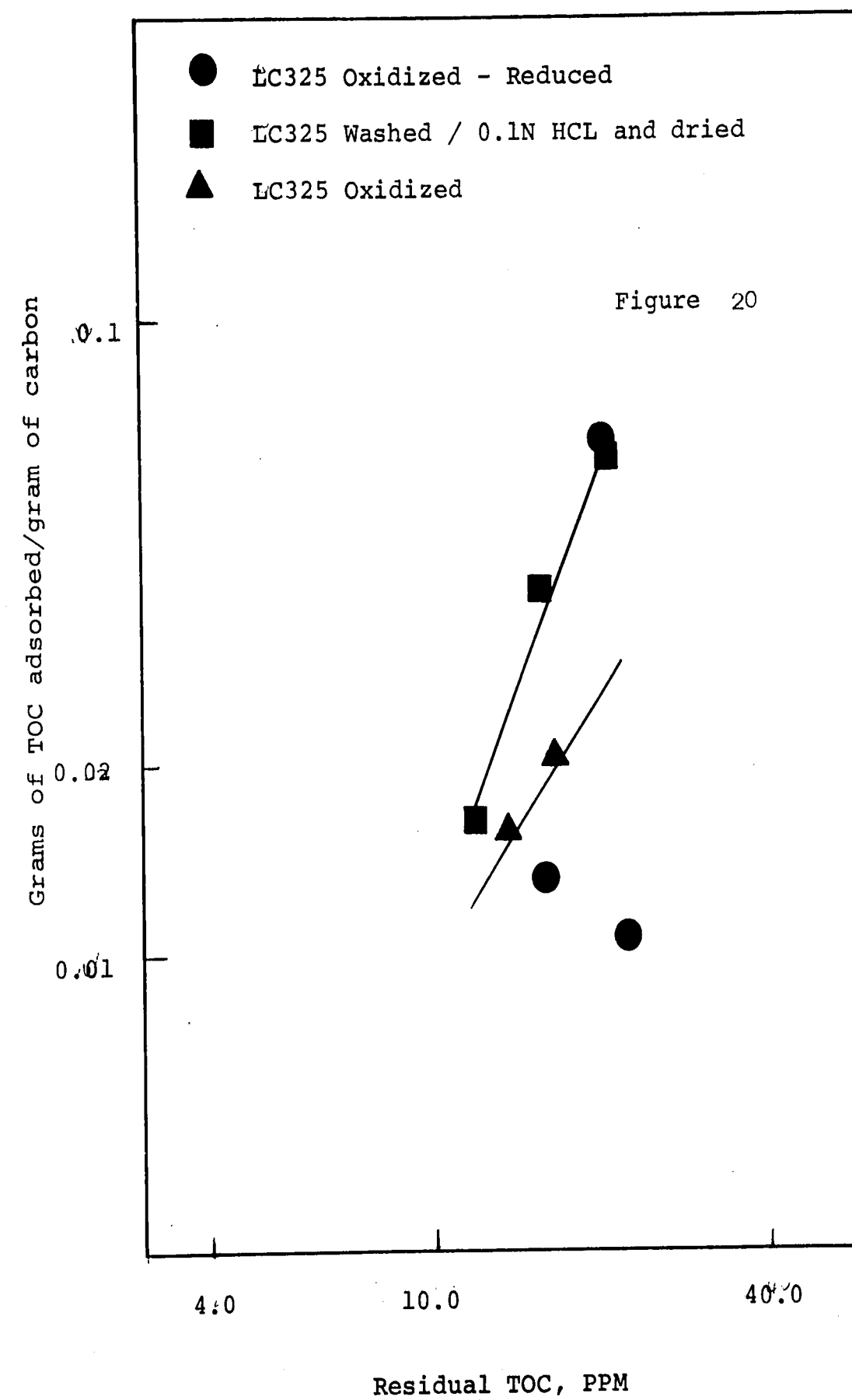
Adsorption Isotherm of TOC from secondary effluent
Darco S51 Carbon



Adsorption Isotherm of TOC from secondary effluent.
Black Pearl P607 Carbon



Adsorption Isotherm of TOC from secondary effluent.
Columbia LC325 Carbon



ADSORPTION OF DEXTROSE ON LC325 WASHED

SVOL 50.0 ml.
 GCPSVOL 1.0 gram
 TEMPERATURE..... 30.0 °C
 OSUGC..... 40.085 grams/ liter

Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ Gram	Equilibration Time Hours
205.7	842.5	0.5
205.7	842.5	1.0
205.7	842.5	1.50
205.7	842.5	2.0
205.7	842.5	4.0
205.7	842.5	6.0
205.7	842.5	8.0
205.7	842.5	14.0
205.4	855.7	30.0
205.0	874.1	50.0
204.9	882.0	60.0
203.8	934.7	77.0

ADSORPTION OF DEXTROSE ON LC325 WASHED

SVOL 50.0 ml.
 GCPSVOL 1.0 gram
 TEMPERATURE 30.0°C
 EQT. 1.0 hour

Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ gram	C/V Grams Carbon/ Liter
6.85	210	32.18
15.8	320	49.3
24.2	450	53.4
34.76	480	72.1
44.24	560	78.5
95.58	770	123.9
148.2	910	162.2
201.7	1020	198.4
313.4	980	318.2

ADSORPTION

ADSORPTION OF DEXTROSE ON LC325 OXIDIZED

SVOL 50.0 ml.
 GCPSVOL..... 1.0 gram
 TEMPERATURE 30.0°C
 EQT. 1.0 hour
 OXIDATION SAT. -- 3 days

Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ gram	C/V Grams Carbon/ Liter
9.48	80.0	116.9
19.1	160.0	122.7
29.8	180.0	167.7
40.3	210.0	195.7
51.1	220.0	230.1
104.5	320.0	322.8
159.6	350.0	459.1
214.1	400.0	538.4
270.4	440.0	615.0

ADSORPTION OF DEXTROSE ON LC325 OXIDIZED - REDUCED

SVOL 50.0 ml.
 GCPSVOL 1.0 gram
 TEMPERATURE 30.0°C
 EQT. 1.0 hour

Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ gram	C/V Grams Carbon/ Liter
7.37	190.0	39.5
15.8	320.0	49.3
25.3	400.0	62.9
34.2	510.0	67.3
44.5	550.0	80.9
96.9	710.0	137.3
150.1	820.0	182.7
204.6	870.0	234.7
259.1	920.0	281.1

ADSORPTION OF LACTOSE ON LC325 WASHED

SVOL 50.0 ml.
 GCPSVOL 1.0 gram
 TEMPERATURE 30.0°C
 EQT..... 1.0 hour

Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ Gram	C/V Grams Carbon/ Liter
5.02	320.0	15.7
16.05	360.0	44.3
21.7	280.0	76.2
27.1	370.0	74.1
54.7	490.0	110.6
81.9	820.0	99.7
110.1	550.0	199.0
137.2	920.0	149.3
165.3	730.0	226.2
218.9	1940.0	112.9

ADSORPTION OF DEXTROSE ON CF300 WASHED

OSUGC..... 50.0 grams/ liter
SVOL 50.0 ml.
GCPSVOL..... 1.0 gram
EQT..... 1.0 hour
TEMPERATURE 30.0°C

Particle Size Range mm	Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ Gram
2.83 - 3.36	256.99	513.0
2.38 - 2.83	255.15	560.0
1.41 - 1.68	248.0	737.0
1.00 - 1.41	246.2	783.0
0.595 - 0.707	244.4	829.0
0.250 - 0.297	240.9	915.0
0.063 - 0.074	258.2	968.0
0.053 - 0.063	237.5	1001.0

ADSORPTION OF DEXTROSE ON CF300 OXIDIZED

OSUGC 50.0 grams/ liter
SVOL 50.0 ml.
GCPSVOL 1.0 gram
EQT. 1.0 hour
TEMPERATURE 30.0°C

Particle Size Range mm	Residual Conc. Millimoles/ Liter	Amount Adsorbed V Micromoles/ Gram
2.83 - 3.36	273.84	184.0
2.38 - 2.83	273.32	211.0
1.41 - 1.68	273.06	224.0
1.00 - 1.41	272.79	237.0
0.841 - 1.00	272.79	237.0
0.595 - 0.707	272.00	276.0
0.250 - 0.297	271.61	296.0
0.063 - 0.074	270.16	369.0
0.053 - 0.063	269.89	382.0

KINETICS OF DEXTROSE ON CF300 WASHED

SVOL..... 50.0 ml.
GCPSVOL 1.0 grams
TEMPERATURE 40.0°C
PARTICLE SIZE RANGE.... 2.38 - 2.83 mm

TIME (MIN)	RESIDUAL CONC. (GRAMS/ LITER)	
0	50.3	
5	48.4	
10	47.3	
20	46.6	K = 867 Micromoles/ Gram (Hr) ^{1/2}
30	46.3	
40	45.9	
50	45.8	

SVOL 50.0 ml.
GCPSVOL 1.0 gram
TEMPERATURE 0.0°C
OSUGC 49.8 gram/ liter
PARTICLE SIZE RANGE ... 2.38 - 2.83 mm

TIME (MIN.)	RESIDUAL CONC. (GRAMS/ LITER)	
0.0	49.8	
5	48.8	
10	48.1	K = 520 Micromoles/ Gram (Hr) ^{1/2}
20	47.6	
30	47.3	
40	46.7	

KINETICS OF DEXTROSE ON CF300 WASHED

SVOL 15.0 ml.
GCPSVOL 0.5 grams
TEMPERATURE 19.0°C
PARTICLE SIZE RANGE...0.595 - 0.707 mm

TIME (MIN.)	RESIDUAL CONC. (GRAMS/ LITER)
0	50.0
10	45.4
20	44.4 K = 1600 Micromoles/ Gram (Hr) $\frac{1}{2}$
30	44.3
40	44.3

SVOL 15.0 ml.
GCPSVOL 0.5 grams
TEMPERATURE 23.3°C
OSUGC..... 50.0 grams per liter
PARTICLE SIZE RANGE... 1.41 - 1.68 mm

TIME (MIN.)	RESIDUAL CONC. (GRAMS/ LITER)
5.0	47.9
10.0	47.1
23.0	46.4
30.0	46.2
45.0	45.4

KINETICS OF DEXTROSE ON CF300 WASHED

SVOL..... 15.0 ml.
 GCPSVOL 0.5 grams
 TEMPERATURE 19.0°C
 OSUGC 50.3 grams per liter
 PARTICLE SIZE RANGE ... 2.38 - 2.83 mm

TIME
(MIN.)

RESIDUAL CONC.
(GRAMS/ LITER)

0.0
 10.0
 20.0
 30.0
 40.0
 50.0
 60.0

50.3
 48.3
 47.9
 47.3
 46.9
 46.7
 46.5

K = 666 Micromoles/
 Gram (Hr)^{1/2}

KINETICS OF DEXTROSE ON CF300 OXIDIZED

OXIDATION..... 0.8 molar - 4 days
 SVOL 15.0 ml.
 GCPSVOL..... 0.5 grams
 TEMPERATURE..... 19.0°C
 PARTICLE SIZE RANGE 2.38 - 2.83 mm

TIME (MIN.)	RESIDUAL CONC. (GRAMS/ LITER)
----------------	----------------------------------

0.0	50.1
5.0	49.6
10.0	49.2
20.0	49.0
30.0	48.7
40.0	48.6

K = 312 Micromoles/
 Gram (Hr)^{1/2}

OXIDATION..... 0.4 molar - 4 days
 SVOL 50.0 ml.
 GCPSVOL..... 1.0 grams
 TEMPERATURE 17.5°C
 PARTICLE SIZE RANGE 2.38 - 2.83 mm

TIME (MIN.)	RESIDUAL CONC. (GRAMS/ LITER)
----------------	----------------------------------

0.0	50.2
5.0	49.2
10.0	48.6
20.0	48.3
30.0	48.3
40.0	47.9
50.0	47.9

K = 432 Micromoles/
 Gram (Hr)^{1/2}

KINETICS OF DEXTROSE ON CF300 OXIDIZED

OXIDATION 0.4 molar - 4 days
SVOL 50.0 ml.
GCPSVOL 1.0 gram
TEMPERATURE 0.0°C
PARTICLE SIZE RANGE 2.38 - 2.83 mm

TIME
(MIN.)

RESIDUAL CONC.
(GRAMS/ LITER)

0.0

50.2

5.0

49.3

10.0

48.9

20.0

48.6 K = 392 Micromoles/
Gram (Hr)^{1/2}

30.0

48.3

40.0

47.9

50.0

47.9

THE ADSORPTION OF UREA FROM AQUEOUS SOLUTION
BY COLUMBIA ACTIVATED LC325 CARBON

Nelson Malwitz and Charles Burchett

Background

Today, a great deal of effort is being expended to learn the functioning and causes of malfunctioning of the innumerable parts of the human body. Also, unprecedented strides are being taken in the research and development of equipment designed to replace and perform the tasks of defective, injured, or dangerously inefficient organs.

On the list of organs which relatively often malfunction is the kidney. As is well known, a man can live normally with 50% kidney efficiency, i.e., one healthy kidney. However, if kidney efficiency is reduced to less than 10%, wastes will accumulate in the body at a sufficient rate and cause death in a week to 10 days.

About a half a century ago, the first artificial kidney machine was successfully used. Today, there are a number of different artificial kidney designs - each with countless variations.

Almost all of the artificial kidney designs rely on the phenomenon of osmosis for their operation. The patient's blood is passed on one side of a semi-permeable membrane while simultaneously a specially

prepared dialysate solution is contacted on the other side.

One idea which may improve the design of the artificial kidney is to re-cycle the dialysate rather than to use a batch process. This feature would allow the dialysate to more closely resemble the composition of the blood. Conceptually, this would tend to make the operation more reversible, thus reducing the harshness of the artificial kidney by approximating the function of the natural kidney.

With the above idea, experiments were performed to determine if urea - a primary human waste - would be adsorbed by carbon.

The Experiments

Experiments were performed to determine the adsorptive capacity of carbon for urea in aqueous solution. Typical urea concentrations found in the blood of the kidney were used.

Solutions with known urea concentration were equilibrated with different measured amounts of carbon for an equilibrium time of one-half hour. Residual and initial concentrations of urea were determined from standard spectrophotometric methods. (18)

Results

As seen in Figure 21, the washed Columbia activated IC325 carbon at an intermediate concentration of 40 mg/100 ml. showed an adsorptive capacity of about 13 milligrams of urea per gram of carbon. However, the addition of acidic oxide groups to the carbon surface enhanced the adsorptive capacity (at the same concentration) by about a factor of 3.0 on a per gram basis.

Discussion of Results

With the knowledge of the characteristics of the two different carbon surfaces, these results might be expected. Urea, a highly polar molecule, would predictably have a greater affinity for the polar acidic oxide groups on the oxidized carbon's surface than for the non-polar characteristics of the surface of washed carbon.

For use in the proposed artificial kidney arrangement (Figure 22) the urea concentration of the uremic person is 100 mg/100ml. To reduce the amount of urea in an uremic person to a safe concentration of 20mg/100 ml. would require about 667 grams of washed carbon or 222 grams of oxidized carbon.

Assuming that the average person has 2.5 liters of blood, the following calculations represent approximately the amount of carbon needed:

$$\frac{(100 - 20) \text{ mg. urea}}{100 \text{ ml. of blood}} \times 2500 \text{ ml. of blood} \times$$

$$\frac{1}{(3 \text{ mg. urea adsorbed / g. of carbon})} = 667 \text{ g.. of washed carbon}$$

OR

$$\frac{667 \text{ g.. of washed carbon}}{3} = 222 \text{ g.. of oxidized carbon}$$

The difference in the amount of oxidized carbon required may or may not be enough to offset the cost of its manufacture for this application. However, for use in a waste treatment project, the economics for the oxidized carbon might be more favorable.

Adsorption Isotherm of Urea on activated carbon (Columbia LC325) in aqueous solution at 30.0 °C for 0.5 hours equilibrium time on a per gram basis

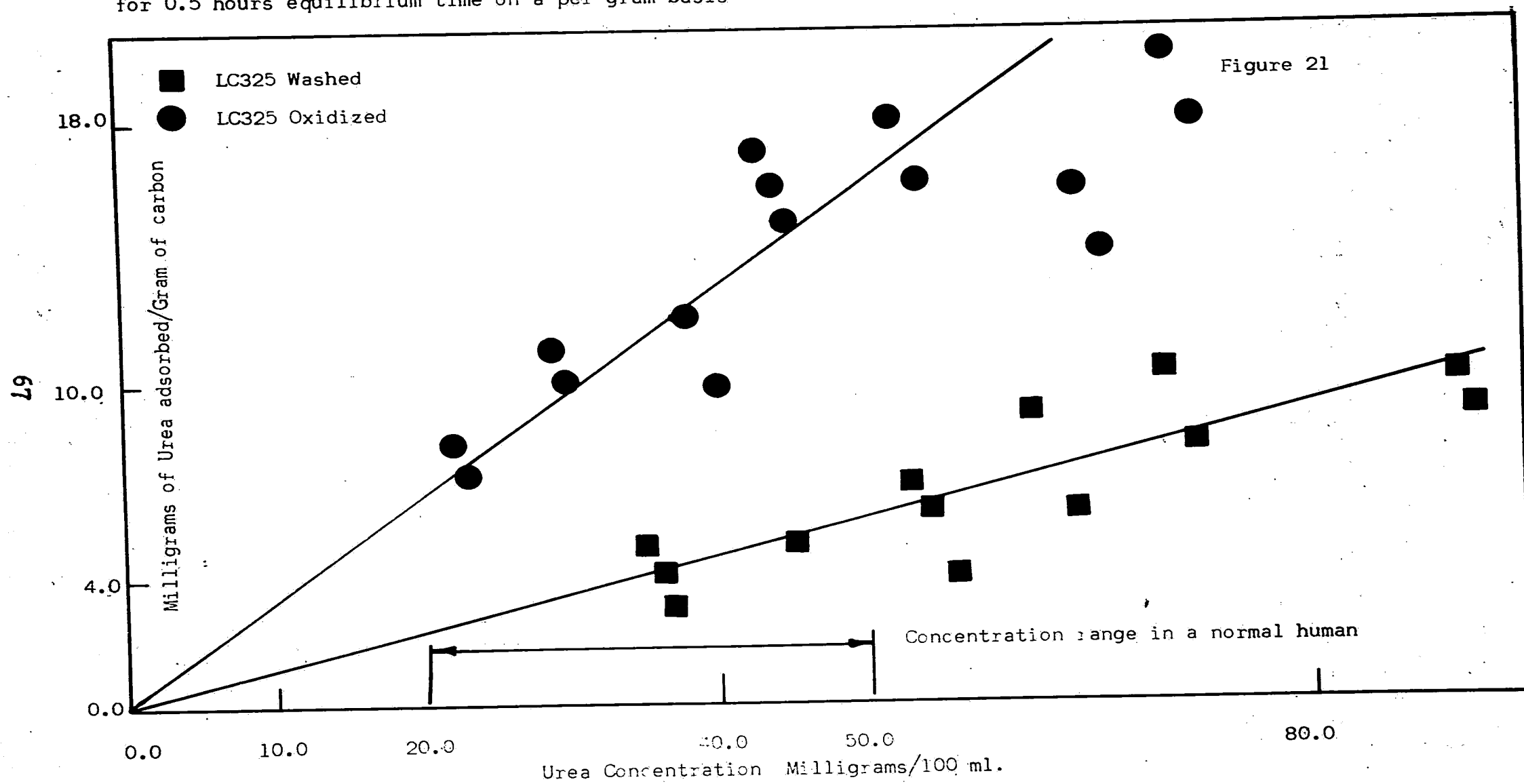
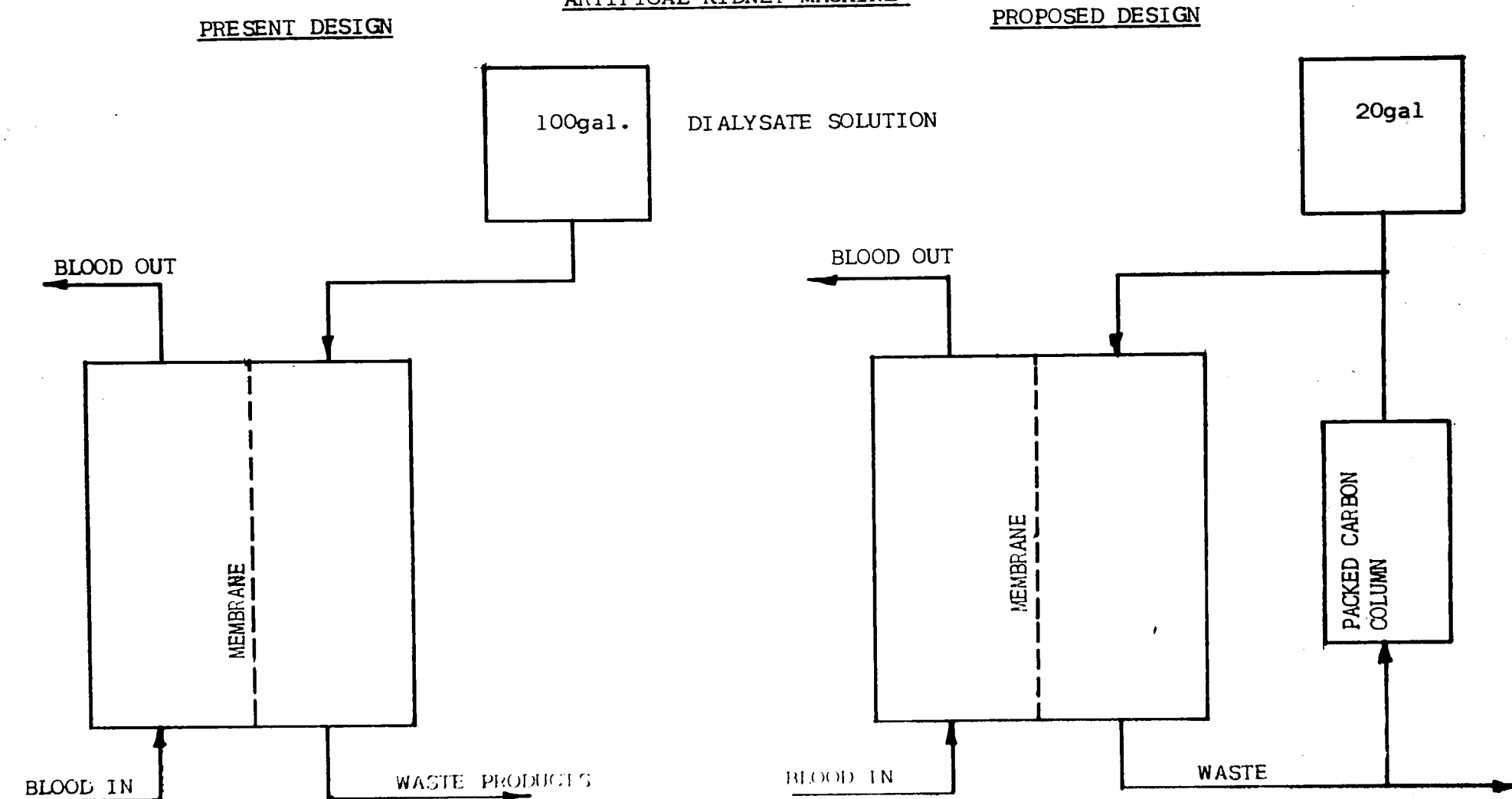


Figure 22

ARTIFICIAL KIDNEY MACHINE



BIBLIOGRAPHY

1. Boehm, Dr. H. P., "Functional Groups on the Surfaces of Solids," Angewandte Chemie, Vol. 5, No. 6., p.p. 533-622, (June, 1966).
2. Bond, G. C., "Catalysis by Metals," . , Academic Press, New York (1962).
3. Boudart, M., "Kinetics of Chemical Processes," p. . , Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1968).
4. Coughlin, R. W. "Carbon As Adsorbent and Catalyst," I. & EC Prod. Res. & Dev., Vol. 8., p. 12, Am. Chem. Soc. (March, 1969).
5. _____, and F. S. Ezra, "Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon," Environmental Science & Technology, Vol. 2, p.p. 291-297, Am. Chem. Soc. (April, 1968).
6. Dedrick, R. L., and R. B. Beckmann, "Kinetics of Adsorption by Activated Carbon from Dilute Aqueous Solution," Phys. Adsorp. Proc. & Princ., Chem. Eng. Prog. Symp. Ser.
7. Eisley, A., and F. Bolinsky, Chem. Eng. Stud., Lehigh Univ., Bethlehem, Pa., Class of 1970.
8. Friedman, L. D., FMC Corp., Res. & Dev. Cen., Princeton, New Jersey, private communication.
9. Kipling, J. J., and C. G. Gasser, "Adsorption from Liquid Mixture at Solid Surfaces," J. Phys. Chem., 64, 710 (1960).
10. Moore, W.A., F. J. Ludzak, and C. C. Ruchhoft, "Determination of Oxygen-Consumed Values of Organic Wastes," Anal. Chem. 23: 1297 (1951).
11. Sawyer, C. N. and P. L. McCarthy, "Chemistry for Sanitary Engineers," McGraw-Hill, New York (1967).

12. Tan, R. N., M.S. thesis, Lehigh Univ., Bethlehem, Pa. (1968).
13. Thomas, J. M., and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, New York (1967).
14. U.S. Dept. of Interior, Office of Coal Research, "Investigation of the Use of Coal for Treatment of Sewage and Waste Waters," Rep. No. 12, Con. No. 14-01-0001-348, Rand Dev. Corp., Cleveland, Ohio (1965).
15. Weber, W. J., Jr., "Kinetics of Adsorption on Carbon From Solution," J. Sanit. Eng. Div., 89, SA2, (April, 1963).
16. _____, and J. C. Morris, "Equilibria and Capacities for Adsorption on Carbon," J. Sanit. Eng. Div. Am. Soc. Civil Engrs. 90, SA 3, 79 (1964).
17. _____, "Adsorption in Heterogeneous Aqueous System," J. A. W. W. A. 56, 447, (April, 1964).
18. "Standard Procedures for Spectrophotometric Chemistry," Urea Nitrogen Method U-10A, p. 1-5.

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